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Graphite Fiber Surface Treatment to Improve Impact Strength and Fracture Resistance in Subsequent Composites

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Graphite Fiber Surface Treatment to Improve Impact Strength and Fracture Resistance in Subsequent Composites

SUMMARY

Carbon fibers have relatively low impact strength when put into composites made from high modulus resin systems. Impact strength can be improved, however, shear and compressive strengths are reduced, by having fibers poorly bound to the matrix resin. It is desirable to maximize these physical properties while maintaining good adhesion of fiber to matrix. One possible solution is to attach elastomeric polymer molecules to the fiber surface. The elastomer should have pendant epoxy groups for attachment to the matrix resin. The elastomer would absorb, and by micro-movement, dissipate stress energy ahead of a forming fracture front. This would prevent filament breakage and travel of the front along the fiber-matrix interface.

One approach to implement this hypothesis was to synthesize elastomers with epoxy groups attached either by grafting or by chemical reaction or regeneration. Four elastomers containing from 0.3% to 1.62% oxirane oxygen (-C-C-) were chosen for



application to Type AS4 carbon fiber. The four elastomers had backbones of ethylene oxide-epichlorohydrin copolymer, ethylene-propylene-diene terpolymer, ethylene-propylene copolymer, and polybutadienediol. These materials were applied from solvent solution to the fiber, then Hercules 3501-5A resin was applied as hot melt to make a prepreg tape, and the tape laminated into 0°, and 90° plies. The results (Table 3) showed all fibers gave low adhesion with no improvement of impact strength even though flexural properties were good. The solution-sized fibers were very difficult to handle, so this approach to elastomer incorporation was stopped.

Polystyrene latex particles that are surface modified with a cationic charge were picked up by and bound ionically to an anionic surface on a pulp fiber. Oxidized carbon fiber surface at pH >7 is anionic. A polystyrene hard resin cationic latex was prepared using epichlorohydrin quaternized diallylmethylamine as

the surface modifier. Exposure of carbon fiber to this latex at pH 10 gave considerable coverage, as shown by scanning electron microscopic photographs, with $\sim 0.5 \mu$ latex particles. Since the particles (spheres) also had epoxy groups on the surface, they would bind to the matrix resin. Efforts were then made to prepare a cationically surface-modified elastomer polymer latex. This was accomplished, except the elastomer spheres coalesced and bridged the filaments so that the fiber strands were stiff and very difficult to separate for prepreg preparation. At this point, the work stopped. The principle of cationic latex attachment to carbon fiber was shown, but a more firm, cross-linked elastomer that would not coalesce and bridge the filaments was not defined.

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Abbreviations Used:

Epi - epichlorohydrin
DMF - dimethylformamide
TEGDMH - tetraethyleneglycol dimethacrylate
SM - surface modified
SML - surface modified latex

INTRODUCTION

High modulus fibers, such as carbon and graphite fibers, suffer from relatively low impact strength and toughness when put into composites made from high modulus resin systems such as typical aerospace epoxy resins. Impact strength of such composites can be improved by utilizing fibers that bond poorly to the matrix resin. However, poor fiber bond strength results in low composite shear and compressive strengths, and related mechanical properties. It is desirable to achieve good impact and toughness while maintaining good adhesion. A method was pursued in this work that is potentially able to achieve this combination of properties.

Previous work (1) has shown the feasibility of modifying carbon fiber surfaces to provide specific monomeric and polymeric types of groups at the fiber surface in a reasonably controlled amount. The objective was to provide char-forming moieties reacted in a controlled fashion on the fiber surface. A logical extension of the chemistry and techniques involved in this work was to substitute, for the char-forming groups, polymeric compounds which have the ability to absorb fracture energy, and thus promise to enhance the toughness, transverse strain, and impact strength of carbon fiber/epoxy composites.

When a mechanical stress is applied to a fiber-reinforced resin composite, stress concentrations are generated at the high modulus-low modulus bridge, or fiber-resin interface. In parallel-fiber bundles in such a composite, the stress concentrations between filaments cause a developing fracture to follow this interface parallel to the fiber surface until the accumulated fracture energy becomes great enough to break filaments. Because of the high stress concentration at the resin-fiber interface, this appears to be a logical place to concentrate energy absorbing materials to reduce the severity of the stresses generated ahead of a fracture front and help to dissipate the front.

APPROACHES

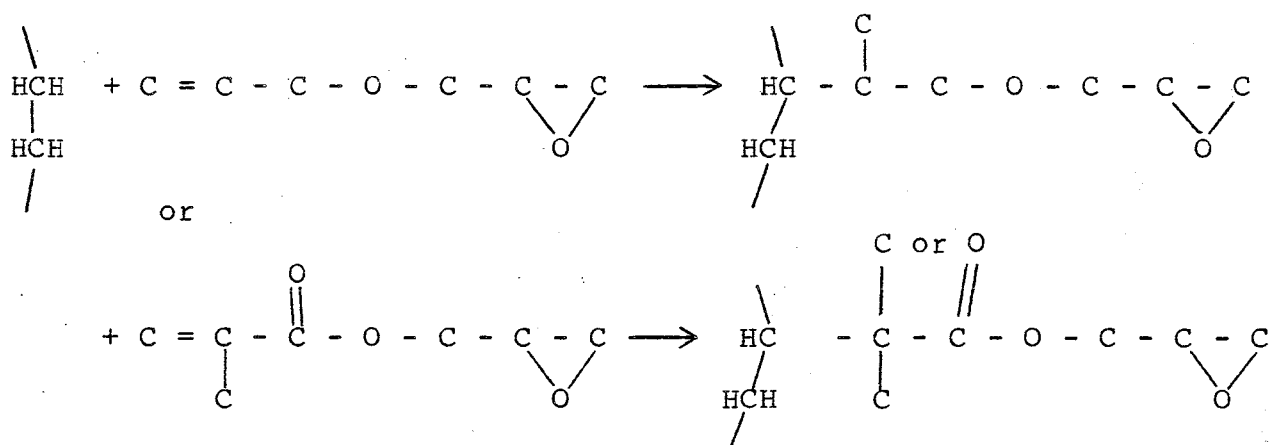
Two general approaches were used. The first utilized the fact that carbon fiber surfaces commercially available are surface treated to provide functionality that will react readily with, and adhere well to epoxy resins. This reactivity was utilized to modify the fiber surface in an attempt to combine good adhesion and also high energy-absorbing capability. It has been shown that dual-functionality modifiers can be prepared that will adhere well to surface-treated carbon fibers. It has also been shown that good adhesion to a highly-surface-treated fiber can be retained, in the presence of "islands" of modifiers, by incorporating diepoxides with the modifiers. Thus a surface treated fiber surface can potentially be tailored using a reactive sizing composed of a high-impact, epoxy-functional modifier and a diepoxide; the ratio of modifier-to-diepoxide should govern the chemistry and adhesion of the modified fiber surface. It is anticipated that the amount and type of modifier in the sizing, and reacted with the fiber surface, will govern the toughness and impact strength of the composite. If sufficient diepoxide bridges are also present, the adhesion-sensitive mechanical properties should be maintained. Several energy-absorbing modifiers were synthesized. These included a variety of different types of polymers, some relatively high modulus, some rubbery. All can potentially undergo high elongation during loading. All of the modifications were expected to result in multiple glycidyl ether or glycidyl ester termination of the particular polymer. Adhesion to the fiber and to the composite laminating resin was through these terminal epoxide groups.

The second approach utilized the fact that polystyrene latex particles around $0.3\ \mu$ in diameter that are cationically charged are extracted from the latex and electrostatically held on anionic pulp fibers. These latices are prepared using cationic polymers as stabilizers. The latex spheres held ionically on an anionic carbon fiber also need to be epoxy functional to react with the base epoxy resin used in the laminating process. To accomplish this, epichlorohydrin was used to quaternize the nitrogen in the cationic polymer to give both cationic charge and epoxy function on the latex particle. In addition, instead of the rigid polystyrene latex used in paper pulp processing, an elastomer latex with the cationic and epoxy modification is needed to absorb fracture energy in the laminate structure.

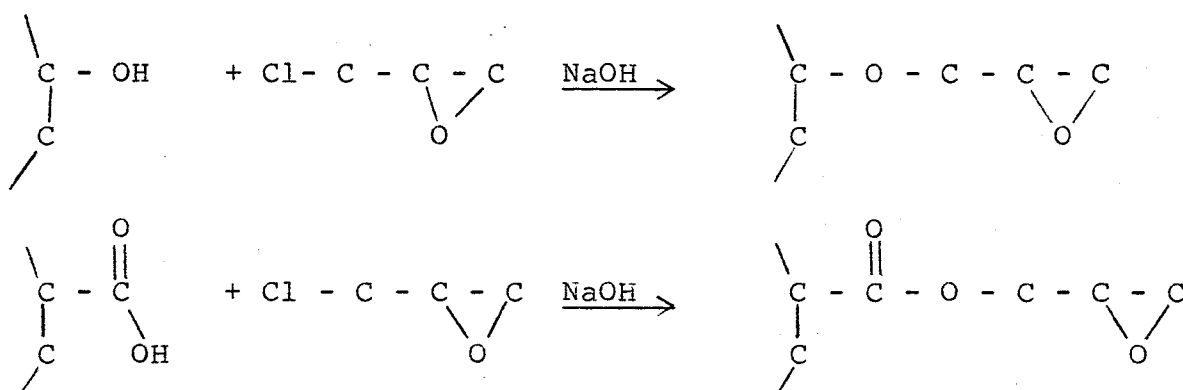
EXPERIMENTAL

First Approach

Three general types of reactions were used to incorporate epoxy functionality into polymeric materials. They were, first free radical (peroxide) grafting of allyl glycidyl ether or glycidyl acrylate onto the polymer (2).



Second, epichlorohydrin was reacted with polymers containing hydroxyl or carboxyl groups.



Thirdly, the regeneration of epoxy groups in epichlorohydrin polymer and copolymer.



A summary of the epoxy modified polymers prepared is given in Table No. 1. Four of these polymers were selected to size AS4 carbon fiber for laminate preparation.

X22575-75 Ethylene oxide - epichlorohydrin copolymer epoxide

To 60 g. of Herchlor C (ethylene oxide - epichlorohydrin copolymer) in 500 ml of chlorobenzene was added 5 g. of NaOH in 15 ml water. The mixture was stirred at 95°C for 4 hours, cooled, and poured into 500 ml of n-decane. The rubbery solid was filtered off, washed with n-decane, and air dried. It was then tumbled in a RotoVac at 40°C at 20 mm for 4 hours. 72 g. of grey rubbery solid was obtained. It analyzed 1.62% oxirane oxygen. 0.5 g. of this polymer was soluble in 10 ml DMF at 40°C and at 22°C; in 10 ml of chlorobenzene at 40°C but cloudy at 22°C; and in 10 ml of trichloroethylene at 40°C, but some insoluble at 22°C.

X22575-77 Glycidyl methacrylate g. ethylene-propylene-diene terpolymer

To 50 g. of ethylene-propylene-diene terpolymer (Aldrich #18,964-2, Mooney viscosity 30) in 500 ml of chlorobenzene was added 15 g. of glycidyl methacrylate and 2 g. of benzoyl peroxide. The solution was stirred at 80°C for 4 hours, cooled, and poured into hexane. The gelatinous mass that separated was recovered by pouring off the hexane, stirring with fresh hexane, and then pouring it off. The soft rubbery solid was air dried over the weekend. It was then slurried with acetone, filtered, and dried in a RotoVac at 40°C at 20 mm for 4 hours. 59 g. of opaque, white rubbery solid was obtained. It analyzed 1.38, 1.43% oxirane oxygen and was soluble at 0.5 g/20 ml in chlorobenzene and trichloroethylene, not in DMF or methylene chloride.

X22575-78 Glycidyl Methacrylate g. ethylene-propylene copolymer

As above (-77), 50 g. of ethylene-propylene copolymer (Aldrich #18,962-6, Mol Wt 170,000; 70% ethylene; Mooney Viscosity 30) in 500 ml of chlorobenzene was reacted with 15 g. of glycidyl methacrylate and 2 g. of benzoyl peroxide. 58 g. of white, opaque, rubbery solid was obtained. It analyzed 0.81% oxirane oxygen. It had the same solubility as -77.

To 75 g. of polybutadienediol (Aldrich #19,079-9) (Mol Wt 2800) in 600 ml of DMF was added 50 g. of epichlorohydrin. The solution was stirred at 90-95°C for 4 hours. Then a solution of 5 g. NaOH in 30 ml of water was added dropwise. The mixture was stirred for 3 hours at 95°C, cooled, and poured into 1L of water. The viscous oil that separated was dissolved in toluene, water washed several times, and dried over anhyd. Na₂SO₄. The solution was then filtered and stripped on the RotoVac at 40°C at 20 mm, leaving 76 g. of viscous yellow liquid. It analyzed 0.27, 0.30% oxirane oxygen. It was soluble only in trichloroethylene.

Sizing Applications

Use of the epoxy-modified rubber compounds as sizings, applied directly to the fiber from solvents which dissolved the compounds, gave sized fibers that were too well consolidated. The individual filaments could not be separated for subsequent impregnation by the base epoxy resin. Addition of Dow's DER 330 epoxy resin to the sizing solutions, to make sizes containing 50% rubber modifier and 50% DER 330 improved the fiber handling characteristics considerably. All sized fibers made from 0.75% and 1.125% size solutions with 50% modifier 50% DER 330 were soft and pliable, and individual filaments could be readily separated; they were also readily wetted by acetone indicating that solvent preimpregnation would be feasible.

Sizing contents of AS4 fiber sized with the four compounds selected for further work were determined by extracting the sized fibers with tetrachloroethylene (TCE) as follows:

<u>X22603-</u>	<u>Sizing Composition</u>	<u>Fiber Handling Character</u>	<u>% Size Extracted</u>
70-1	0.75 g X22575-77; 0.75 g DER 330; 298.5 g TCE	Soft, slight tack	1.29
70-2	1.125 g X22575-77; 1.125, DER 330; 297.7 g TCE	Slightly stiff, slight tack	1.38
70-3	0.75 g X22575-78 0.75 g DER 330; 298.5 g TCE	Soft	0.67
70-4	1.125 g X22575-78; 1.125 g DER 330; 297.75 g TCE	Very slight stiffness	0.48
70-5	0.75 g X22575-79; 0.75 g DER 330; 298.5 g TCE	Slightly stiff	0.37
70-6	1.125 g X22575-79; 1.125 g DER 330; 297.75 g TCE	Slightly stiff	0.43

Previous work (1) used a moderate-property epoxy resin for measuring adhesion to sized fibers. Evidence implied that in many instances the resin was failing and the interfacial bond was not being tested. In the present work it is necessary that the higher-property epoxies be used. Hercules 3501-5A was selected for initial trials. Since it is normally not applied from solution it was necessary to find a solvent for preparing experimental tows. It was found that the hardener can be predissolved in dimethylformamide and the other components in methylene chloride. Mixing the two solutions allows the resin solution to be used directly to preimpregnate the carbon fiber and advance the resin while the solvent is being evaporated. Initial attempts gave resin contents of 208% and 257% which is too high for normal use but can be handled experimentally. The 208% fiber was filament-wound onto a rack and molded into a unidirectional laminate. Some bubbling of the excess resin that flashed from the mold indicated that some DMF remained in the resin. Longer prepreg tower residence times and lower resin contents were tried in an attempt to reduce the residual DMF. Short beam shear strength of these samples were obtained.

Seven sets of AS4 carbon fiber were sized with epoxy-modified rubber compounds (Table No. 2) for preparation of laminates for shear and impact testing. Attempts to size fiber with the epoxy-rubber compounds led to excessively cohesive bundles which would not be suitable for preimpregnation by hot-melt epoxy resin. Consequently, the size compositions were prepared using, as the solids components, 50 parts epoxy-rubber compound and 50 parts DER 330 liquid epoxy to act as a fiber "dispersing" aid in the hot-melt.

Attempts to prepare composites from the hot-melt base resin using prepreg fiber coated from dimethylformamide solution proved too difficult due to handling; evaporation of the solvent was incomplete, leading to excessive bubble formation during resin cure. Short beam shear strength of the solvent-prepared 3501-5A laminates was only about 13,000 psi, well below the anticipated 18,000 psi of typical laminates prepared from hot-melt prepreg. The excess solvent could not be removed in an evaporation tower since increased time or temperature led to excessive polymerization of the resin, to the point that the prepreg was not handleable.

Laminate Preparation and Testing

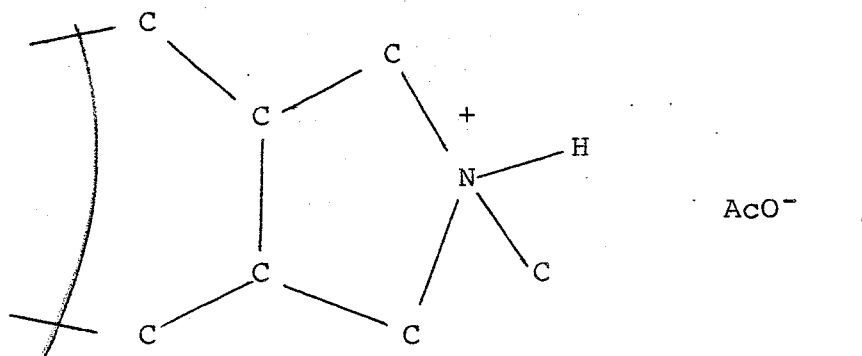
Laminates were prepared from the carbon fibers using the modified rubber sizing compounds reported in Table 2. These used Hercules 3501-5A resin composition applied as a hot-melt to the sized fibers to make a prepreg tape. The tape was then laminated in 0° plies to make nominally 0.080 inch thick laminates for shear and flexure testing, and into alternating 0°, 90° plies to nominally 0.070 inch thick laminates for falling-dart impact testing.

Second Approach

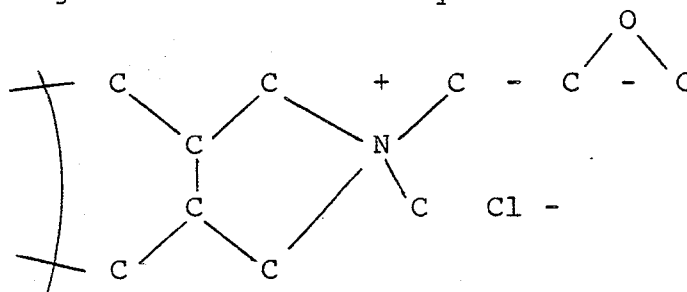
To check the adhesion to carbon fiber, a surface modified styrene latex was quaternized.

X22575-85

Emulsion Hercules S2484A (6030-31) [25.5% total solids, consisting of 90% styrene and 10% of 73.5% acrylamide : 26.5% methylallylammonium acetate (3)] a surface modified latex - 330 g. - was divided into 16 small centrifuge tubes. They were spun at 10,000 rpm for 1 hour, and the clear liquid (monomers and salts) was decanted. Distilled water was added to the original volume, tubes shaken, and centrifuged again. The clear top was decanted and the tubes made up to volume with more distilled water. To the 330 g. of suspension of the surface modified particles of polystyrene,



was added 2 g. NaOH to give pH 10. 5 g. of epichlorohydrin was added and the suspension was stirred at 70°C for 4 hours and then cooled to 25°C. It was then divided into 16 centrifuge tubes and spun at 10,000 rpm for 1 hour. The clear upper layer was discarded. The lower suspension was diluted with distilled water to the original volume. This quaternized latex



was used to treat carbon fiber.

A 12-inch strand (0.25 g.) of AU4 (not surface treated) carbon fiber (XA525-17-20, spool 173) was placed in a 0.0625% styrene latex suspension made up of 0.5 g. of S2484A (25% solids) in 200 ml of distilled water and adjusted to pH 10 with 20% aq. NaOH. The strand was moved around for three minutes, then rinsed three times in distilled water and hung to dry at room temperature. The fiber was labeled X22575-88-1.

A 12-inch strand of AU4 fiber was sized the same way in suspension of 0.065% solids of quaternized latex -85 and 0.005% DER 330. The treated fiber was X22575-88-2.

A 12-inch strand of AS4P carbon fiber was sized the same as 88-1 above. It was labeled X22575-89-3. AS4P was also treated the same as 88-2. It was labeled X22575-89-4.

All four of these treated fibers were soft, not tacky, and the individual fibers separated easily. The scanning electron photomicrographs of the fibers are shown in Figures 1 and 2. 88-1 AU4 had very few latex spheres attached on each fiber. AS4P 89-3 had more and AS4P 89-4 with quaternized latex had the most. These results show that sufficient particle coverage could be accomplished to justify this approach.

Treatment -89-4 was repeated with AS4P fiber and latex -85, but at two higher concentrations.

X22575-93-1	AS4P	0.25%	latex solids + 0.25%	DER 330
93-2	AS4P	0.375%	latex solids + 0.375%	DER 330
93-3	AU4	0.375%	latex solids + 0.375%	DER 330

All of these strands were somewhat stiff, but individual fibers could be separated and had a soft hand. Photomicrographs of these fibers are shown in Figures 3, 4, and 5. They show few spheres on 93-1, 93-2 about the same but more small spheres. 93-3 with AU4 shows some globules, but many large agglomerates.

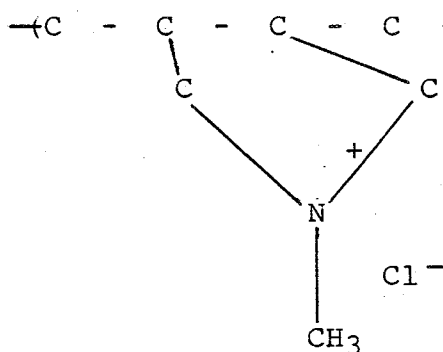
This surface-modified polystyrene latex (-85) with the epichlorohydrin group added to quaternize should be cationic at pH 10. An electrophoretic mobility test on this latex used above showed a charge of zero at pH 10.5. This result indicated that more possible cationic sites were needed on the latex particle surface. To do this, a SML was made with 90% styrene and 10% methyldiallylammonium acetate, instead of the 10% of 73.5% acrylamide -26.5% methyldiallylammonium acetate used in -85. This would give four times more cationic sites.

To 16.2 g. of polydiallylmethylamine hydrochloride (30.9% in water) in 58 ml of distilled water at 92.94°C with stirring in a Morton flask under N₂ was added a solution of 1.4 g. of ammonium persulfate in 5.3 ml of distilled water at a rate of 1.5 ml per hour with a syringe pump about 3.5 hours. During the same time period, 50 g. of styrene was added dropwise. The white latex was stirred for an additional 15 minutes at 92° after the additions were completed. It was cooled and filtered through a 100 mesh screen. 126 g. of white latex was obtained. The latex was 42% solids and had a particle size of 0.6 micron measured by log

absorbance vs. wavelength (370-350 nm) plot. This SM latex was reacted with epichlorohydrin under acid conditions - pH 6 - at 25°C for 16 hours. Electrophoretic mobility measurements were made on the SM latex and on its epichlorohydrin modified form.

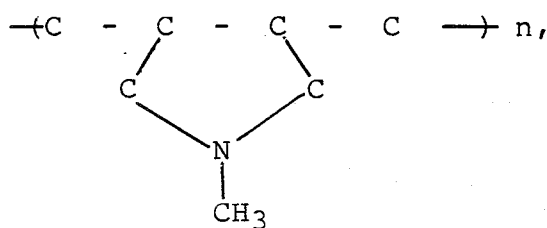
	pH	Charge
SM Latex-22)	5.2	+3.0
"	10.5	-0.95
Epi-SM Latex (-23)	5.9	+3.4
"	10.5	0

The SM latex modifier, $\text{-(C - C - C - C -)}_n$, was cationic as expected below pH 7.

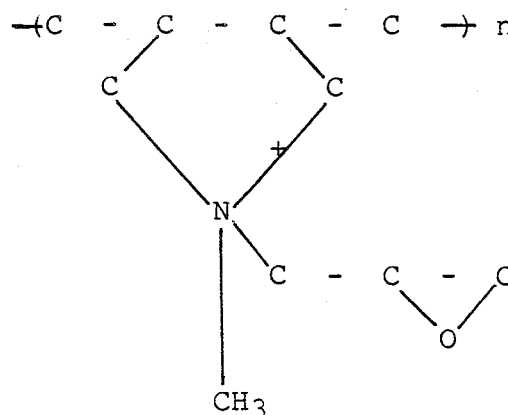


and

neutral,



(or slightly anionic) at pH above 7. The epi-modified SM latex should be cationic both below and above pH 7, i.e.,



It was neutral above pH 7, indicating little or no quaternization.

Samples of AU4 and AS4P carbon fiber were treated at 0.25% of the two latices at pH 6 so the particles would be in cationic form.

X23033-25-1 SM Latex (-22)	AU4 fiber
-2 "	AS4P fiber
-3 Epi-SM Latex (-23)	AU4 fiber
-4 "	AS4P fiber

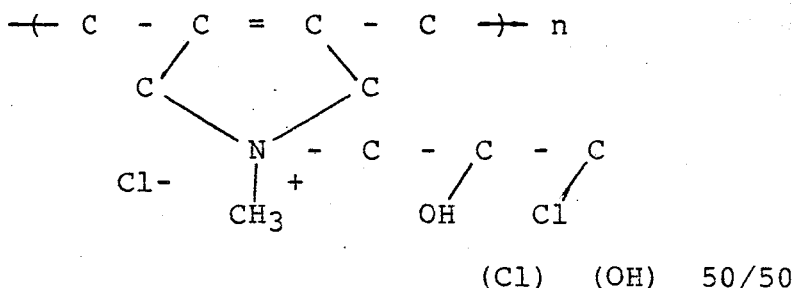
The fibers were given one water rinse after the bath treatment. After drying their hand indicated the strands were all slightly stiff, but the fibers separated well and were fairly soft. The scanning electron microscope photographs are attached. The surface of 25-1 and 25-2 appear to have more spherical and ovoidal particles than 25-3 and 25-4. Fiber 25-2 probably had the greatest number of particles; 25-3 and 25-4 had considerable agglomerated coating in chunks between fibers. There were some agglomerates on 25-1. (Figures 6, 7, 8, 9)

To obtain the quaternary salt modified latex, which can be used above pH 7, where the carbon fiber would be anionic, $\sim\text{C-O-}$, the SM latex -22 was reacted with epi at 90°C for 1 hour and 1 mold of NaOH was added continuously throughout the 1 hour period. The final pH was 8.5 for the epi-SM latex (-38). Its electrophoretic mobility was

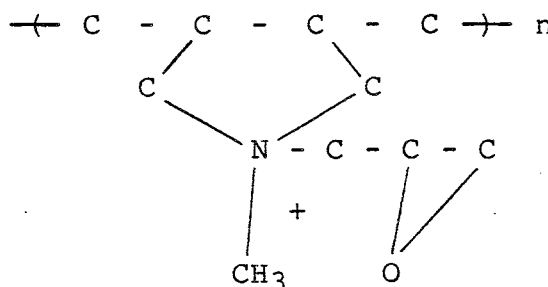
pH 6 + 3.2

pH 10.5 + 2.5

However, now the latex had agglomerated some with some larger particles now present. As a second approach to a quaternary modified, diallylmethylallylammonium chloride was polymerized and converted to the chlorohydrin, i.e.,

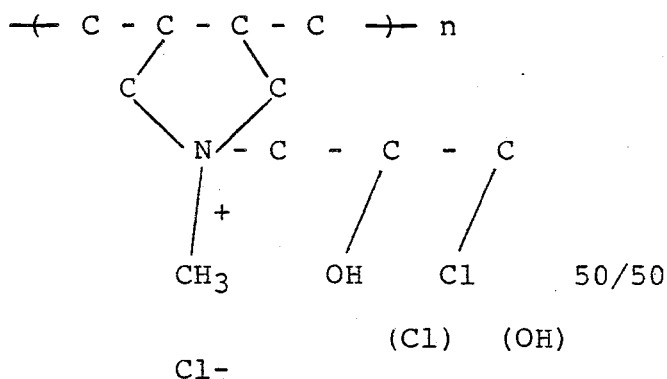


and this was polymerized with styrene to give the SM latex (39);
at pH>7 it should be

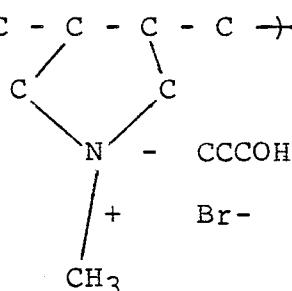


The carbon fiber contains an oxidized surface. It would be nonionic below pH 7 and anionic above pH 7. So the greatest deposition of latex particles should be above pH 7 with cationic (quat) charge on the particles.

The SM latex (-22) was reacted with epichlorohydrin at 90°C for 1 hour with 1 M of NaOH added continuously throughout. The final pH was about 8.5 for the epi-modified latex (-38). Its electrophoretic mobility was +3.2 at pH 6 and +2.5 at pH 10.5. This material should now coat fibers above pH 7. As a second approach, two SM latices were made with styrene and a preformed quat modifier. They were (-39) with



and (-43) with $\neg C - C - C - C \neg$ n



Measurements on the two were

	<u>Particle Size</u>	<u>pH</u>	<u>Charge</u>
-39	0.32 μ	10.5	+1.98
-43	0.49 μ	10.5	+2.04

Using the 3 latices -38, -39, and -49 with positive mobilities at pH 10, carbon fibers AU4 and AS4P were treated with 0.25% suspensions at pH 10 as follows:

X23033-49-1	Latex -38	AS4P fiber
-49-2	Latex -38	AU4 fiber
-49-3	Latex -39	AS4P fiber
-49-4	Latex -39	AU4 fiber
-49-5	Latex -43	AS4P fiber
-49-6	Latex -43	AU4 fiber

The scanning electron microscope photographs are shown in Figures 10 and 11; 49-1 and -2 show scattered coverage, 5 and 6 are almost devoid of particles, 49-3 and 49-4 show good coverage by 0.5 μ particles with almost no agglomerates. The conclusion is that the epichlorohydrin modified quat latex is the one to use.

To have more of an elastomer latex than the hard resin styrene used in the above, butylacrylate/acrylonitrile SMLs were prepared. These were done with persulfate emulsion polymerization at 92°C using 90/10 butylacrylate/acrylonitrile (4) with 10% polydiallylmethylammonium chloride as the modifier. The latex was a stable emulsion 0.5 μ particle size and 24% solids. Isolation (acetone precipitation) of the polymer gave a rather soft, tacky elastomer. To get a more firm rubber, the preparation was repeated using tetraethyleneglycol dimethacrylate (TEGDMA) as cross-linker. The ratio was 90/10/0.5 butylacrylate/acrylonitrile/TEGDMA. It gave a stable latex and the isolated elastomer was very firm. This preparation was repeated using the other modifier.

A surface modified latex was prepared from a mixture of 90/10/0.5 parts of butylacrylate/acrylonitrile/TEGDMA (tetraethyleneglycol dimethacrylate) with 10% of the polymerized quaternary diallylmethylchlorohydropropylammonium chloride as the surface modifier. Unlike the t-amine modifier, this quat gave considerable agglomeration during the polymerization. The agglomerates were filtered off, leaving a thick emulsion but with only 14% solids instead of the expected 25%. This acrylic rubber when isolated was a firm, stiff elastomer. The latex emulsion had a particle size of 0.5 μ and an electrophoretic mobility of +2.12 at pH 10 - ideal values. This emulsion was -89.

Carbon fibers were treated with -89 latex. A 0.25% emulsion was made in distilled water adjusted to pH 10 by addition of 5% aq. NaOH.

2A) A 12 inch strand of AU4 carbon fiber was dipped in the emulsion, swirled around for 3 minutes, withdrawn, and hung to dry at 25°C.

2B) A 12 inch strand of AS4P fiber was dipped in the same emulsion in the same way.

2C) A 12 inch strand of AU4 fiber was dipped in a fresh 0.25% solids emulsion for 3 minutes, withdrawn, dipped quickly in distilled water (adjusted to pH 10), and hung to dry.

The scanning electron photomicrographs are shown in Figures 12, 13, and 14. A and B fibers were stiff; C was softer. The micrographs show B to have the most coverage, followed by A and C. There was considerable coalescence of the deposits and bridging of the fibers. There were some individual spheres of latex throughout. These fibers were not satisfactory for prepreg preparation.

Further runs quaternizing the acrylic latex with epichlorohydrin were made. It was found that if the NaOH was added at a rate to keep the pH at 6 at 60°C over 7 hours, very little agglomeration of the latex occurred and 90% of the latex was recovered. This run (-14) had mobility of +1.8 at pH 10.

To overcome this coalescence, SM latices were made with 1 part, 3 parts, and 5 parts of cross-linker TEGDMA. The elastomers were isolated from the latices. The one with 1 part TEGDMA was a very firm elastomer at room temperature - definitely a higher glass transition temperature than the 90/10/0.5 elastomer. However, with 5 parts TEGDMA, the elastomer was firm but still elastic at room temperature and not much firmer than the 10/90/1 material. The 1 part and 5 part TEGDMA latices were quaternized with epichlorohydrin under acidic conditions to give materials with electrophoretic mobilities of +1.35 and +1.5, respectively.

Fibers were dipped in 0.25% solids dilution of the above at pH 10, swirled around 60 sec, dipped once in distilled water rinse (adjusted to pH 10), and hung to dry at room temperature. With 0.5, 1, and 5 parts cross-linker, the dry strands were stiff, and the individual fibers were coalesced into a firm bundle. They could be teased apart by hand and were then soft and flexible, but this would not be satisfactory for prepreg preparation.

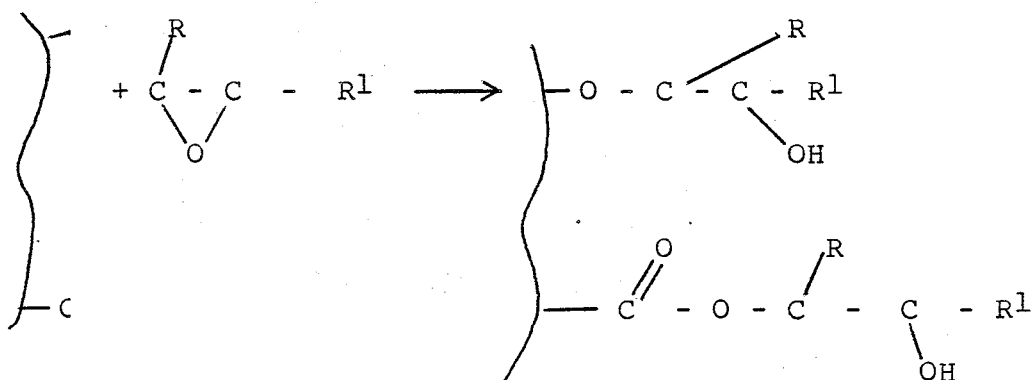
The 5 part latex was again made to 0.25% solids as above, but now the fiber was dipped in 3 distilled water rinses. The dried fiber was no different than with one rinse - stiff and firm strand.

The only treatment that has given soft handling properties with individual fibers separating in the treated strand, has been SM 100% styrene latex with one distilled water rinse. This, of course, is a very hard resin. This would indicate that an elastomer latex is needed that is absolutely hard at room temperature.

DISCUSSION OF RESULTS

lastomeric polymer chain attached to the surface of a carboer should impart impact strength and toughness to compo made from them if the attached polymer bonds poorly to the m resin. These elastomeric polymer chains would have the abili absorb fracture energy that concentrates at the fibern interface. This would prevent a developing fracture from wing this interface parallel to the fiber surface and accumng enough energy to break the filament. The elastomer, poorlnd to the matrix, could undergo micro-slippage to dissithe stress energy generated ahead of a fracture front and e its termination.

approaches were conceived to attach polymeric molecules to cafiber. The fiber surface with an oxidized carbon layer will nt -C-OH and -COOH groups under neutral or acidic condi. These groups will react with oxirane oxygen to form covalonds. Thus, an epoxy group could anchor an elastomer polym the carbon fiber, i.e.,



, a first approach was to attach an epoxy group to an alrearmed polymer chain. This was done by free radical graftf allyl glycidyl ether or glycidyl methacrylate to a nonfunal (chemically) polymer; by reacting epichlorohydrin underc conditions with a hydroxyl or carboxyl containing polymnd by regeneration of epoxy groups in epichlorohydrin polymnd copolymers. These reactions were carried out on fiftelymers. Four of these products were chosen because they were omers and were soluble in trichloroethylene to size carbo fibers.

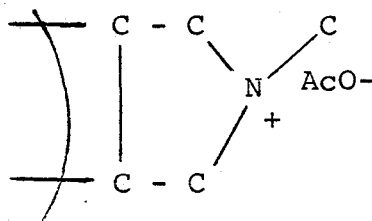
- 75 Ethylene oxide-epichlorohydrin copolymer
epoxide 1.62% oxirane oxygen
- 77 Glycidyl methacrylate g. ethylene-propylene-
diene terpolymer 1.4% oxirane oxygen
- 78 Glycidyl methacrylate g. ethylene-propylene
copolymer 0.81% oxirane oxygen
- 79 Polybutadienediol glycidyl ether 0.3% oxirane oxygen

The sized fibers are listed in Table No. 2.

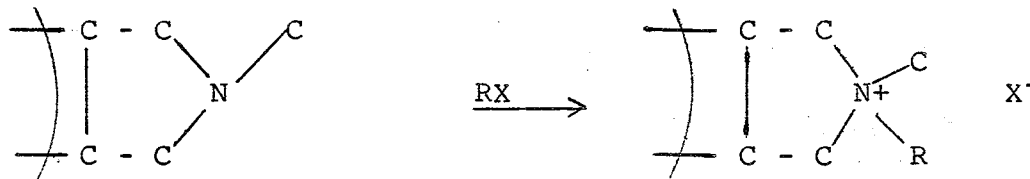
These were prepared using 50 parts DER 330 liquid epoxy added to the 50 parts epoxy elastomer to act as fiber dispersing aid in the hot-melt; without DER 330 excessively cohesive bundles of fibers were obtained.

Laminates were prepared from the sized fibers using Hercules 3501-5A resin applied as a hot-melt to make a prepreg tape. The tape was then laminated in 0° piles to make 0.080" thick pieces for shear and flexure testing, and into alternating 0°, 90° piles for 0.070" thick laminates for falling-dart impact tests. The results (Table 3) show all fibers gave low adhesion. Flexural properties were good, except Sample 5B2 even though it ran readily in the prepreg and laminate operation. Impact results were not improved when the epoxy elastomers were applied as solutions. Because of difficulty in handling the sized fibers, this first approach was stopped in favor of a second approach using surface modified latex deposition.

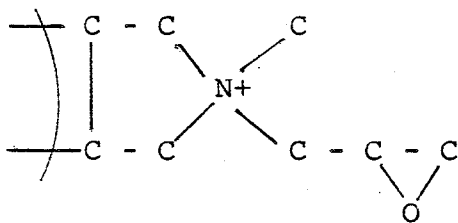
Anionic pulp fibers will remove cationically charged polystyrene particles ($\sim .3 \mu$) from a latex and bind them ionically to the fiber surface. These latices were prepared using tert-amine salt monomer as emulsifier in an emulsion polymerization. Methyldiallylammonium acetate (or chloride) to form a polystyrene latex with a surface charge, i.e.,



Electrophoretic mobility measurements show the latex particles to have plus charge below pH 7 and no charge above pH 7. If, however, these t-amine groups in the latex are quaternized, they then have a plus charge (cationic) above pH 7, i.e.,



If epichlorohydrin is used as the quaternizing agent, i.e.,



the latex particles have a cationic charge and an epoxy function.

At pH 10 where the oxidized carbon fiber surface will be anionic, the cationic latex particles will be ionically bound to the surface. When these fibers are made into a laminate, the epoxy group will form bonds to the matrix resin. If the polymer in the latex is an elastomer, and not a polystyrene hard resin, the desired energy absorption will be obtained when incipient fracture stress is applied.

With epichlorohydrin quaternized surface modified polystyrene latex, good deposition of latex spheres was obtained on carbon fiber (Figure 11). These fibers had good handling properties and separated easily. Attempts were then made to prepare a surface modified latex with an elastomeric polymer in place of the hard resin polystyrene. Butadiene-styrene would not polymerize with the amine modifier present either as t-amine salt or as quaternary salt. Butylacrylate-styrene formed agglomerated latices. Butylacrylate-acrylonitrile formed a SM latex and the polymer was a soft elastomer.

The addition of 0.5 part tetraethyleneglycol dimethacrylate to butylacrylate-acrylonitrile (90-10) gave a firmer elastomer. However, the fibers treated with this latex (Figures 12, 13, 14) show coalescence as though the latex spheres had joined and bridged the fibers. They were stiff and had poor handling properties. The addition of as much as 1 and 5 parts of the TEGDMA cross-linker did not solve this problem, giving stiff firm bundles of treated fibers that were difficult to separate.

CONCLUSIONS

The hypothesis that large elastomer molecules attached to carbon fiber would impart increased impact strength and fracture resistance to subsequently prepared composites was neither proved nor disproved. Solution application of elastomers containing epoxy groups for attachment to the carbon fiber was too difficult to handle and gave sized fibers that were consolidated to the point that individual filaments could not be readily separated.

It was shown that surface modified latex spherical particles of polystyrene hard resin could be attached to carbon fibers by ionic charge. Latices made from soft elastomers gave too much cold flow or coalescence of the particles across individual filaments and gave stiff strands that could not be separated. It would appear that the development of a firm, stiff elastomer latex that is cationically modified and that has rubber characteristics but will remain in discreet particulate form on the fiber surface is necessary. To do this will require further change in polymer composition or cross-link density over those previously examined.

REFERENCES

1. J. T. Paul, Jr. and W. E. Weldy, "Graphite Fiber Surface Treatment to Improve Char Retention and Increase Fiber Clumping", Technical Report NAS1-15869, Final Report, November 1980.
2. A. Ranve and J. T. Khamis, "Studies on Grafting Glycidyl Methacrylate on Polyvinyl Chloride Backbones", J. Polymer Sci 61, 185-94 (1962).
3. G. H. Butler and R. J. Angelo, "Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds", J.A.C.S. 79, 3128-3131 (1957).
4. E. M. Filachione et al, "Preparation and Properties of Acrylic Ester-Acrylonitrile Copolymers", Rubber Age, 1953, 631-637.

Table 1 - Polymer Modifications for Potential Sizings

<u>Designation</u> <u>X22575-</u>	<u>Base</u> <u>Polymer</u>	<u>Modifying</u> <u>Reactant</u>	<u>Modifier</u> <u>Catalyst</u>	<u>Reaction</u> <u>Solvent</u>	<u>Product</u> <u>Analysis</u> <u>% Oxirane</u> <u>Oxygen</u>
66-1	Polyvinyl chloride homo-polymer (Stauffer SCC-NV-1)	Allyl glycidyl ether	Benzoyl peroxide	Methyl ethyl ketone	0.32
67	Vinylchloride/vinylacetate/vinyl alcohol, 91%/3%/6% (Aldrich #18,299-0)	Epichlorohydrin	Sodium hydroxide	Dimethyl formamide	0.05
69	Polypropylene (Pro-fax 6501)	Allyl glycidyl ether	t-Butyl perbenzoate	Chlorobenzene	0.15
70	Carboxylated polypropylene	Epichlorohydrin	Sodium hydroxide	Dimethyl formamide	0.73
72	Carboxylated vinyl chloride/vinyl acetate copolymer 83%/13%/1% COOH	Epichlorohydrin	Sodium hydroxide	Dimethyl formamide	0.24
74	Epichlorohydrin homopolymer (Herclor H)	-	Sodium hydroxide	Chlorobenzene	1.26
75	Ethylene oxide/epichlorohydrin (Herclor C)	-	Sodium hydroxide	Chlorobenzene	1.62
76	Carboxylated polyvinyl chloride	Epichlorohydrin	Sodium hydroxide	Dimethyl formamide	0.22; 0.24
77	Ethylene-propylene-butadiene copolymer (Aldrich #18,964-2)	Glycidyl methacrylate	Benzoyl peroxide	Chlorobenzene	1.41
78	Ethylene-propylene copolymer (Aldrich #18,962-6)	Glycidyl methacrylate	Benzoyl peroxide	Chlorobenzene	0.81

(continued)

Table 1 (continued)

<u>Designation</u> <u>X22575-</u>	<u>Base</u> <u>Polymer</u>	<u>Modifying</u> <u>Reactant</u>	<u>Modifier</u> <u>Catalyst</u>	<u>Reaction</u> <u>Solvent</u>	<u>Product</u> <u>Analysis</u> <u>% Oxirane</u> <u>Oxygen</u>
79	Polybutadiene diol rubber (Aldrich #19,079-9; MW 2,800)	Epichlorohydrin	Sodium hydroxide	Dimethyl formamide	0.27; 0.30
80	Ethylene oxide- epichlorohydrin copolymer	Glycidyl methacrylate	Benzoyl peroxide	Chlorobenzene	1.80
81	Polychloroprene (Aldrich #18,168-4)	Glycidyl methacrylate	Benzoyl peroxide	Chlorobenzene	<0.1
82	Styrene-butadiene copolymer (Aldrich #20,054-9)	Glycidyl methacrylate	Benzoyl peroxide	Chlorobenzene	0.20; 0.34
83	Styrene-allyl alcohol copolymer (Aldrich #19,111-6)	Epichlorohydrin	Sodium hydroxide	Dimethyl formamide	0.14

Table 2 - Fibers Sized with Epoxy-Modified Rubber Compounds

<u>X22603- Lot Number</u>	<u>Sizing Composition</u>	<u>Size Content (%)</u>
90-1	1.125 g X22575-77 1.125 g Dow DER 330 epoxy 297.75 g trichloroethylene	1.42-1.62
90-2	1.125 g X22575-78 1.125 g DER 330 297.75 g perchloroethylene	1.78-2.15
90-3	1.125 g X22575-79 1.125 g DER 330 297.75 g perchloroethylene	1.42-1.78
90-4	1.7 g X22575-78 1.7 g DER 330 296.6 g trichloroethylene	2.42-2.51
90-5	1.7 g X22575-79 1.7 g DER 330 296.6 g trichloroethylene	1.83-1.96
90-6	1.125 g X22575-75 1.125 g DER 330 297.75 dimethylformamide	0.84-1.10
90-7	1.7 g X22575-75 1.7 g DER 330 296.6 g dimethylformamide	N.A.

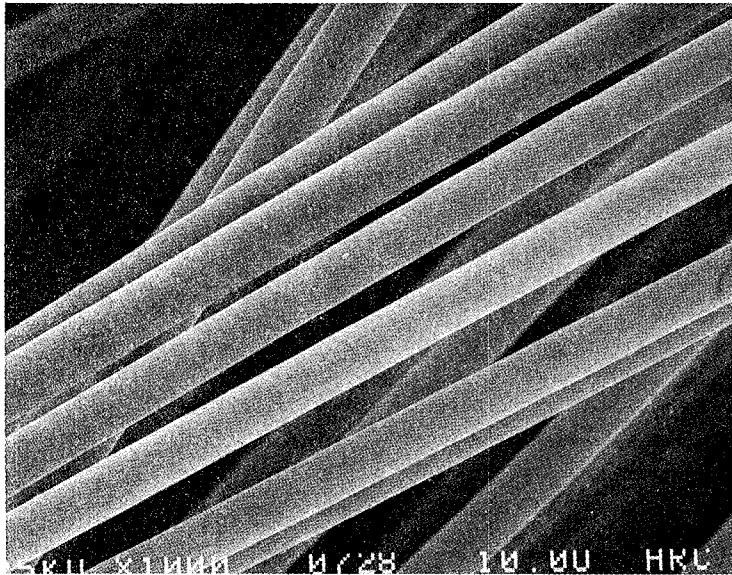
Table 3 - Falling Dart, SBS, & Flexure Properties

<u>Designation</u>	<u>Short Beam Shear (MPa)</u>	<u>Cv %</u>	<u>Strength (GPa)</u>	<u>Cv %</u>	<u>Modulus (GPa)</u>	<u>Cv %</u>	<u>50% failure Probability Falling Dart Impact * (cm-Kg)</u>
X22603-90-1A	42.9	4.9	1.48	2.4	148	7.5	NA
X22603-90-2A1	48.9	7.1	1.52	2.1	146	1.8	29
X22603-90-3A	44.5	7.4	1.64	2.4	162	3.9	44
X22603-90-4B	44.7	2.3	1.46	7.4	150	1.6	55
X22603-90-5B2	30.8	4.8	0.82	4.3	134	9.4	58
26 X22606-90-7	NA	-	NA		NA		41
AS4W Control	Typical 124	5	NA		NA		55
AS4W Control	"	5	NA		NA		50

* Energy to break

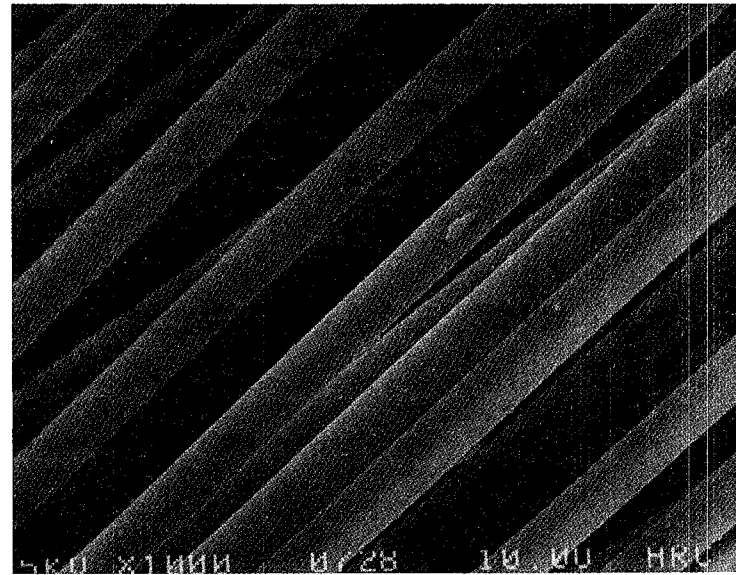
Figure 1 – Treated AU4 Fibers

X22575-88-1



1 Treated with S2484A

X22575-88-2



3 Treated with Epoxidized S2484A

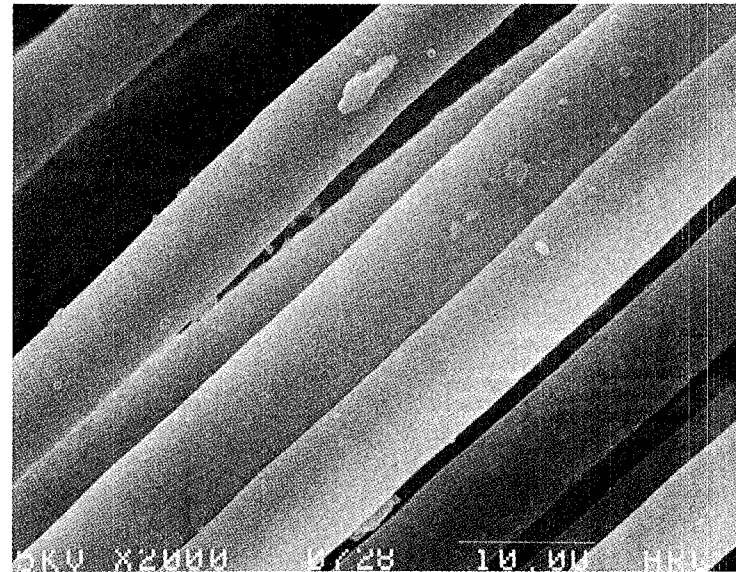
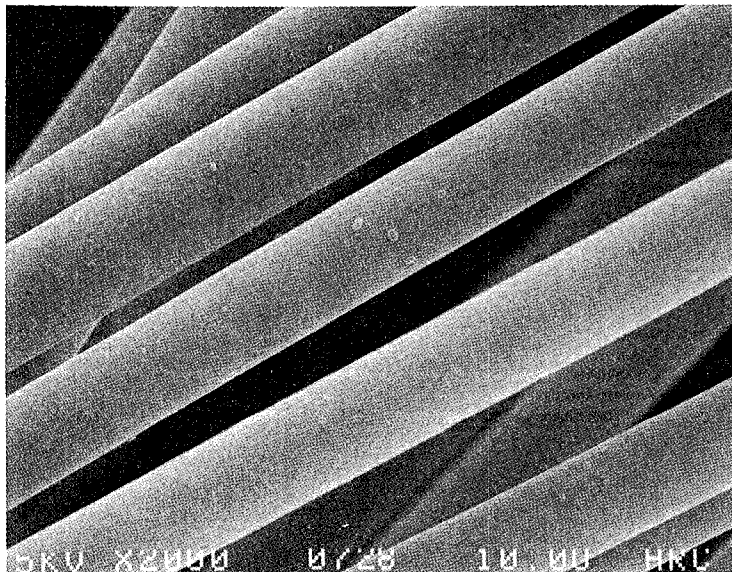
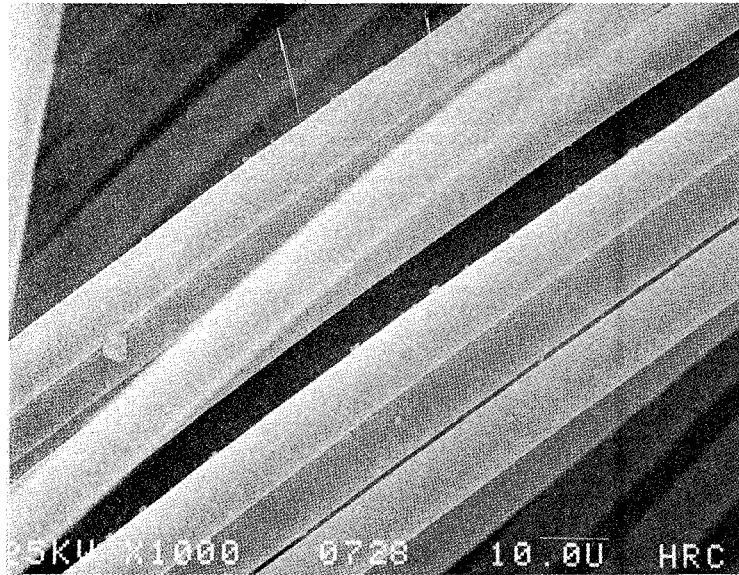


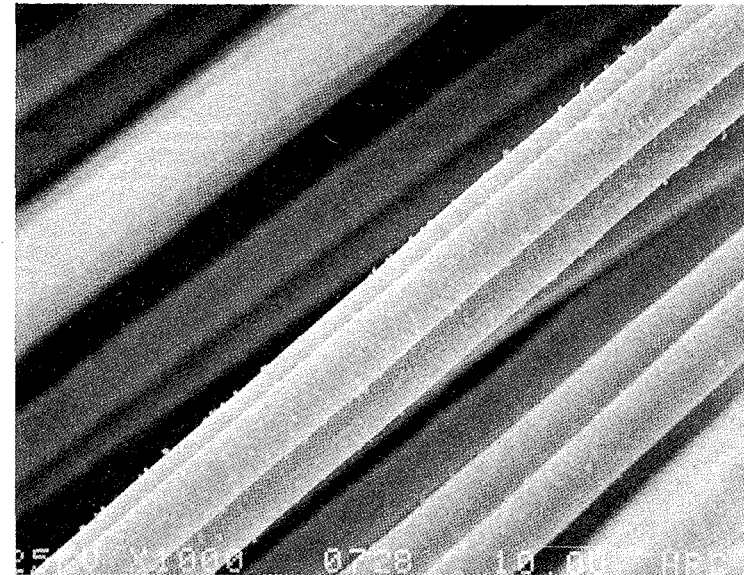
Figure 2— Treated AS4P Fibers

X22575-89-3

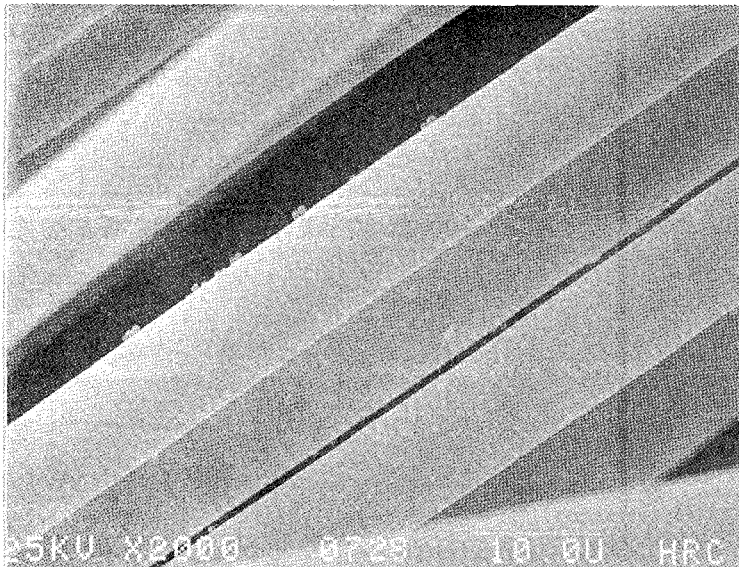


1 Treated with S2484A

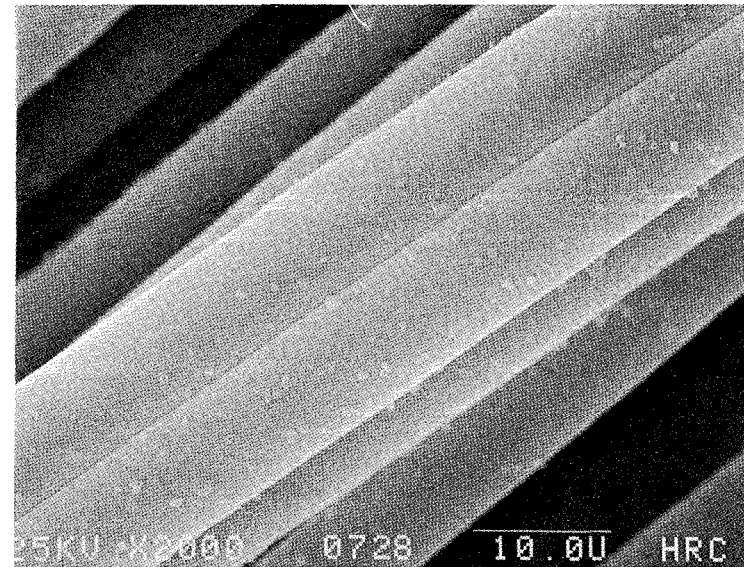
X22575-89-4



3 Treated with Epoxidized S2484A

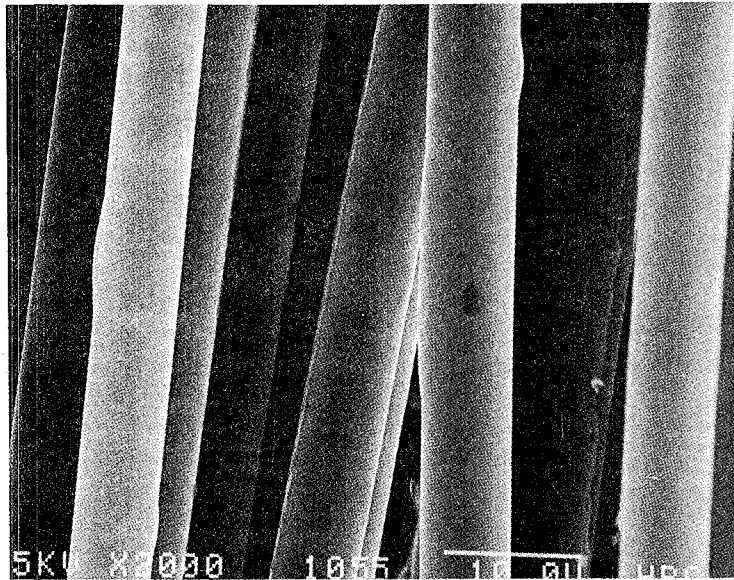


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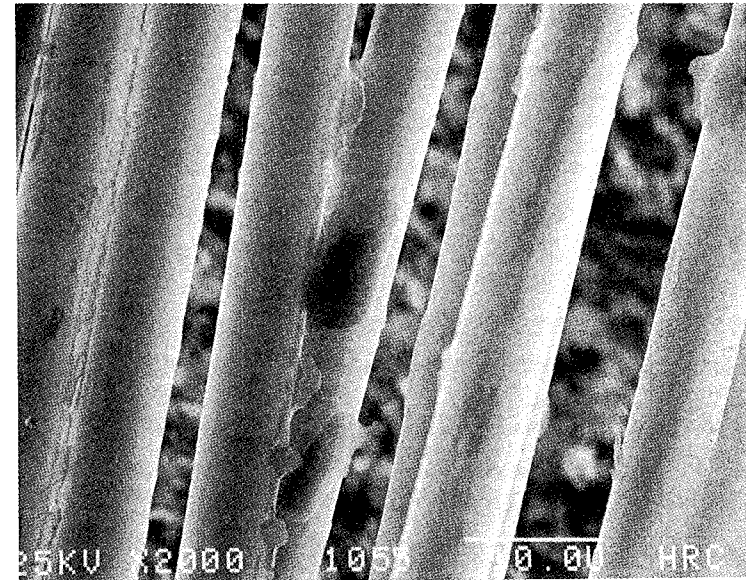


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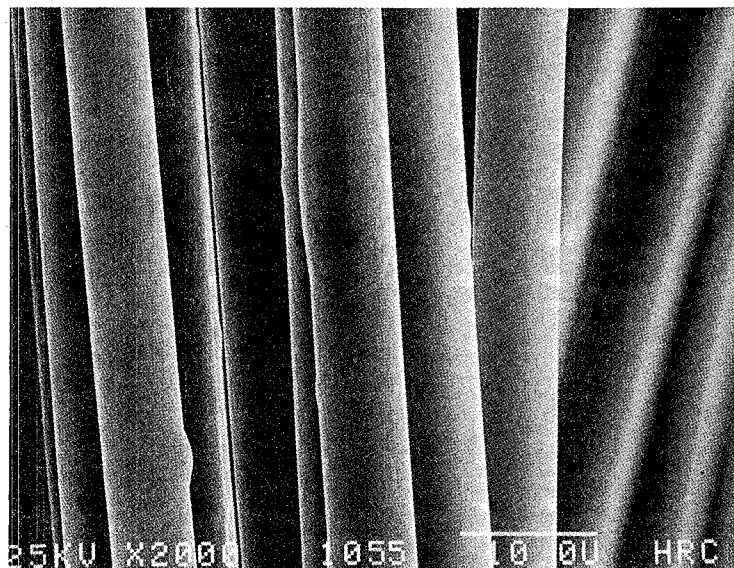
Figure 3— AS4P Treated With 0.25% Latex + 0.25% DER 330



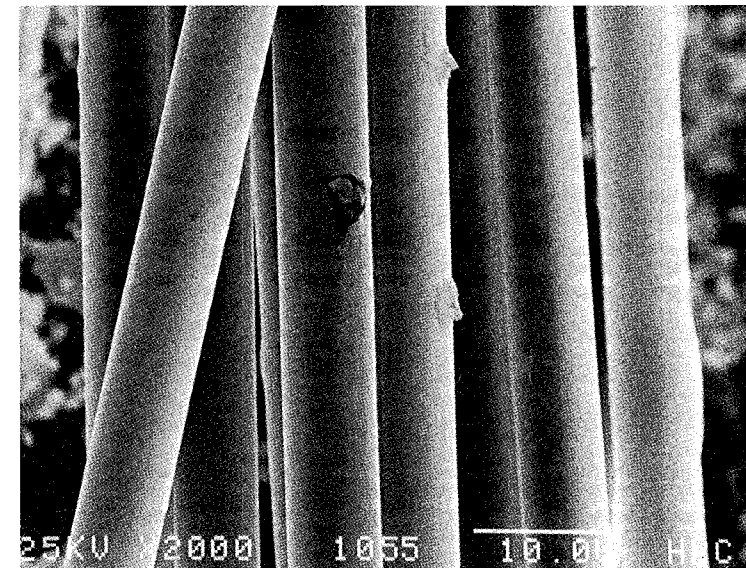
93-1a



93-1b



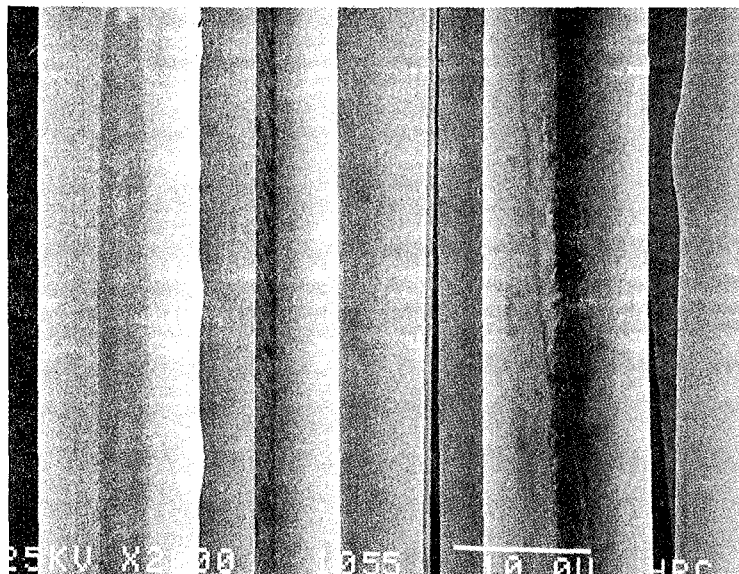
93-1c



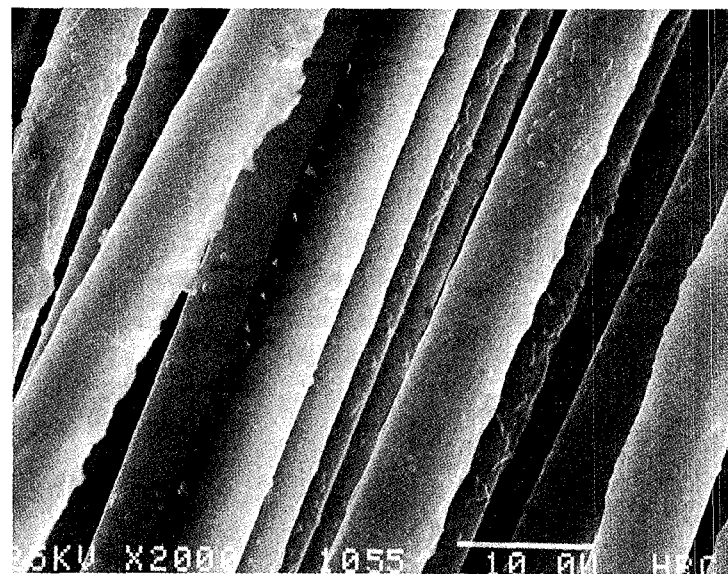
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X22575-93-1

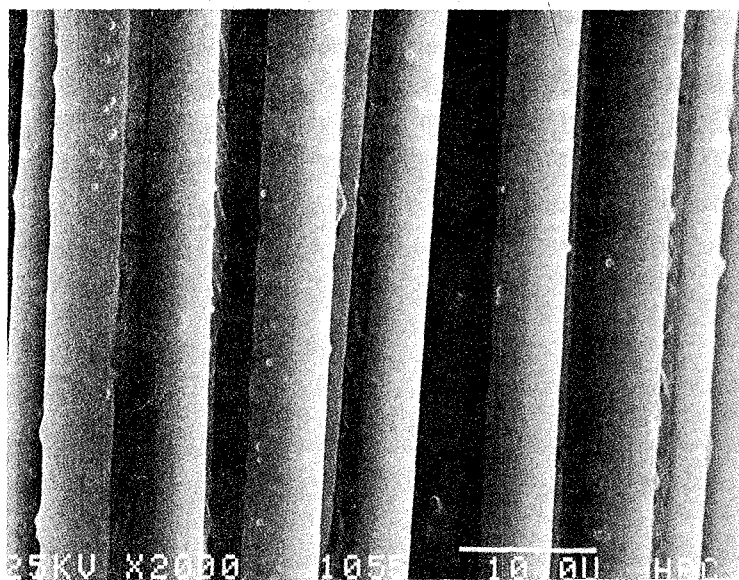
Figure 4— AS4P Treated With 0.375% Latex + 0.375% DER 330



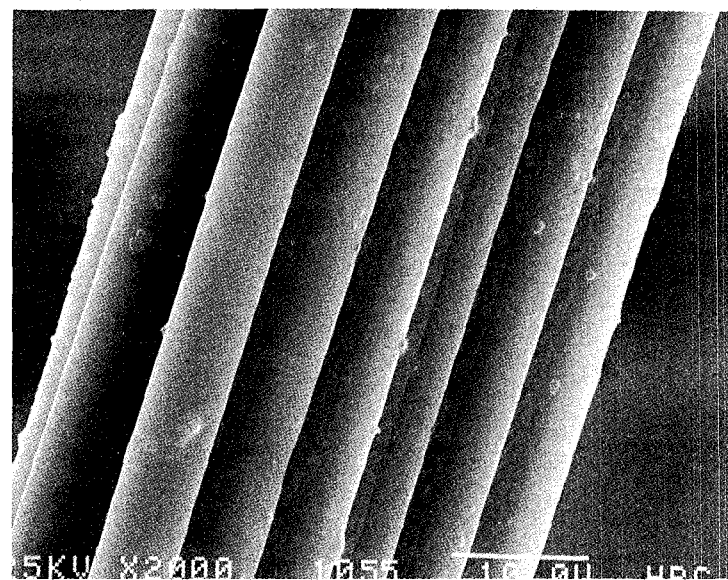
93-2a



93-2b



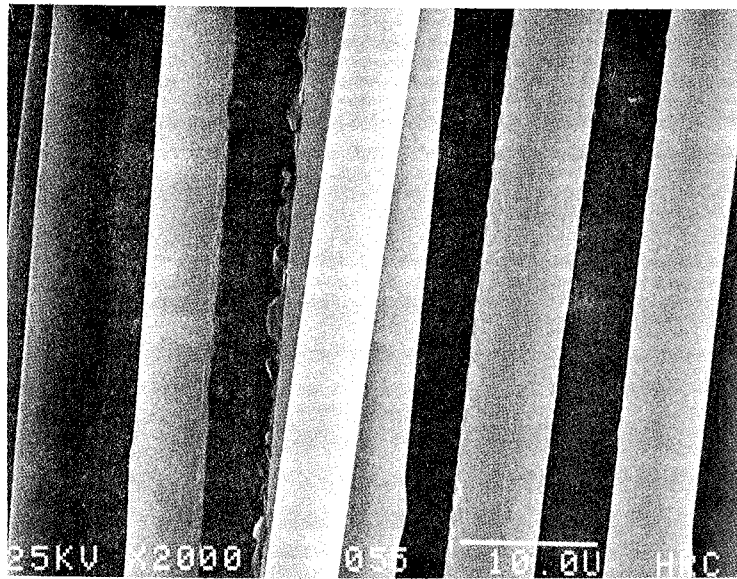
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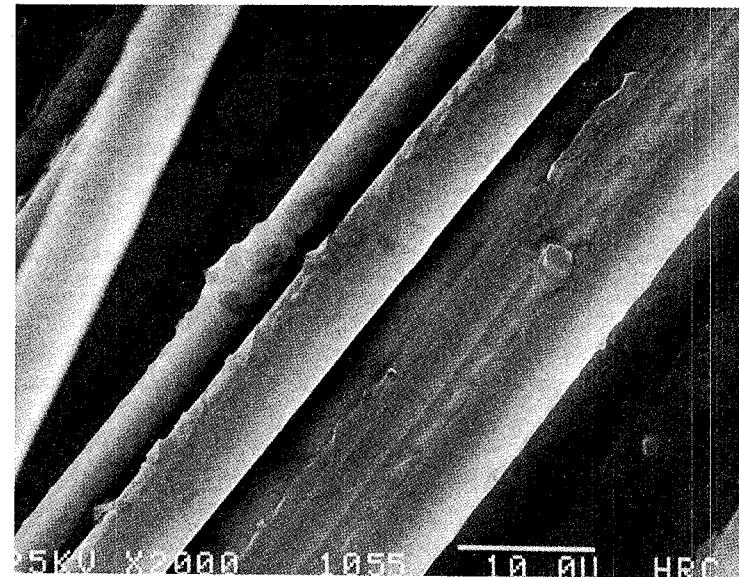
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X22575-93-2

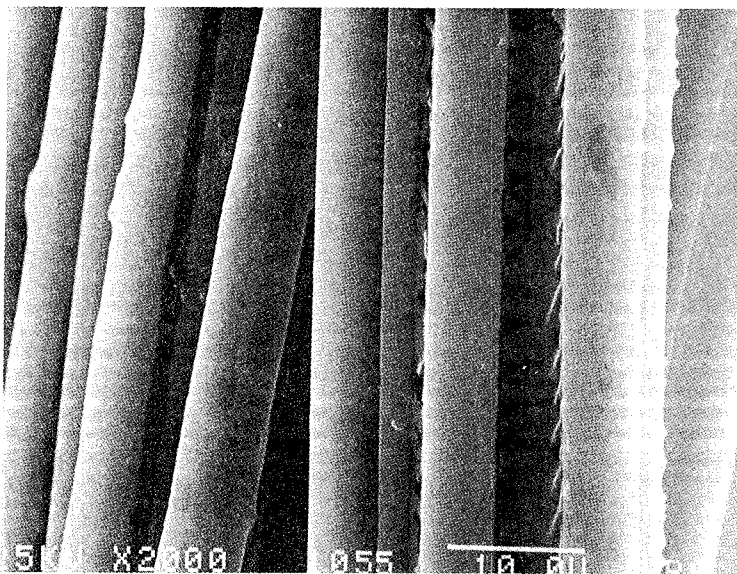
Figure 5— AU4 Treated With 0.375% Latex + 0.375% DER 330



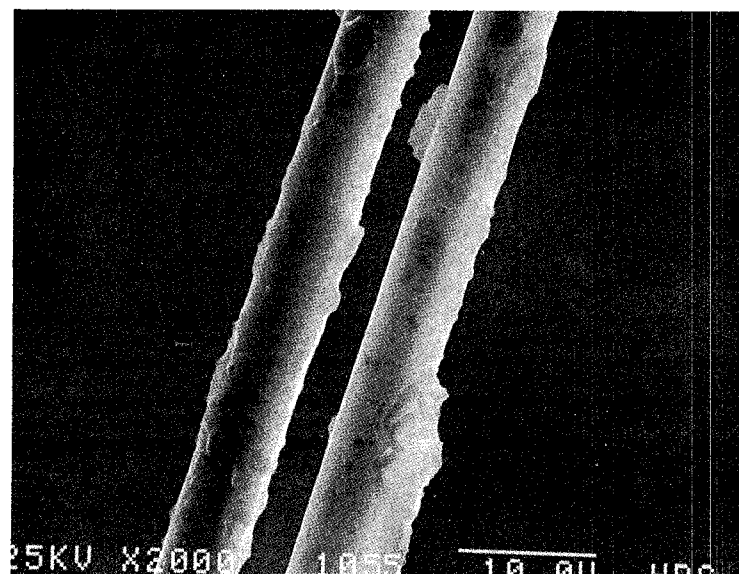
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93-3b



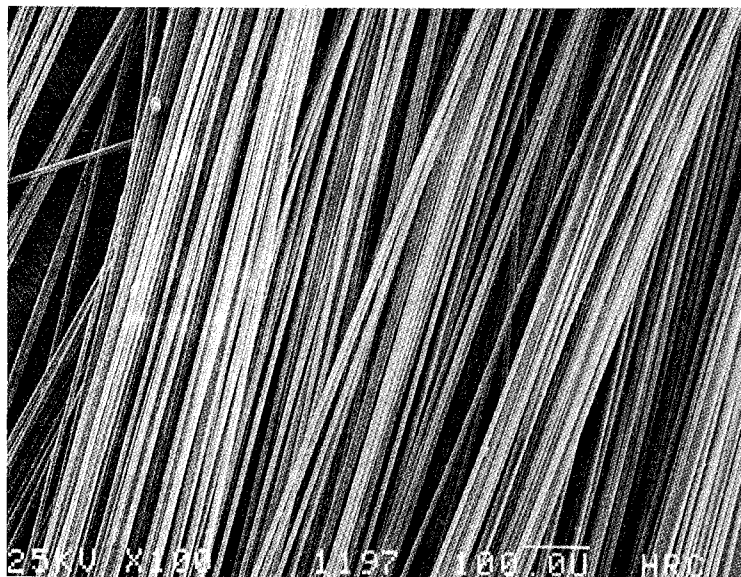
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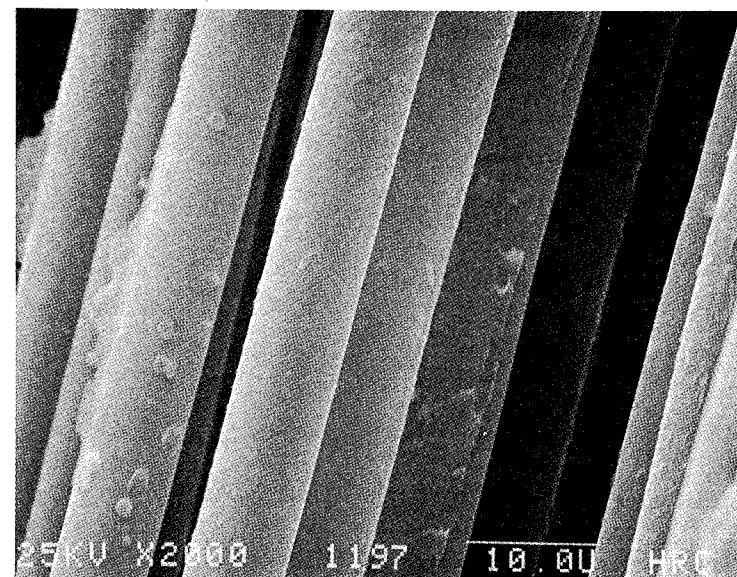
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X22575-93-3

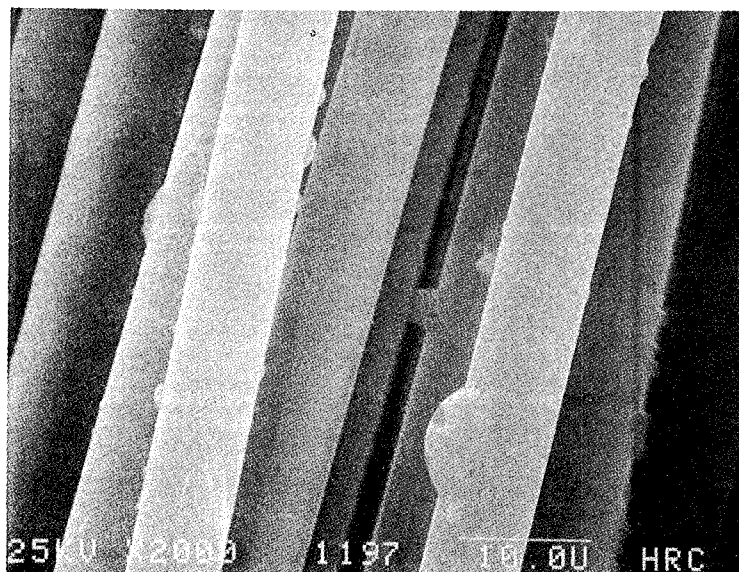
Figure 6-AU4 Fiber Treated With Surface Modified Styrene Latex at pH 6



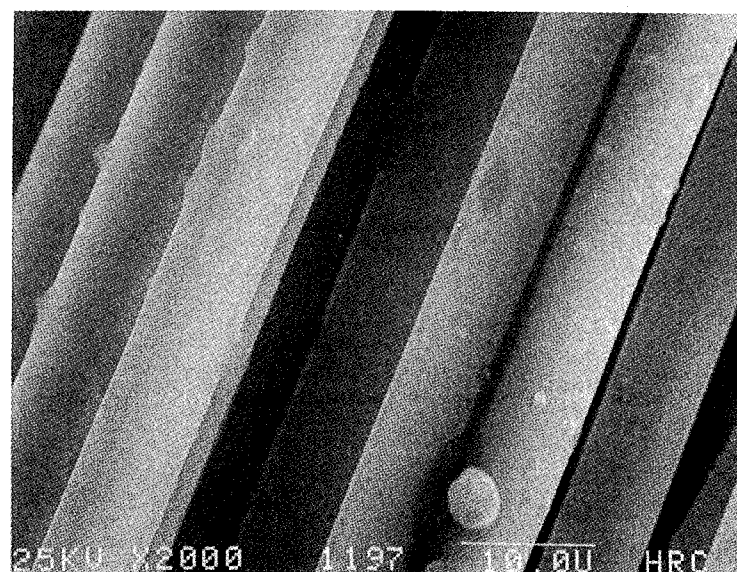
25-1a



25-1b



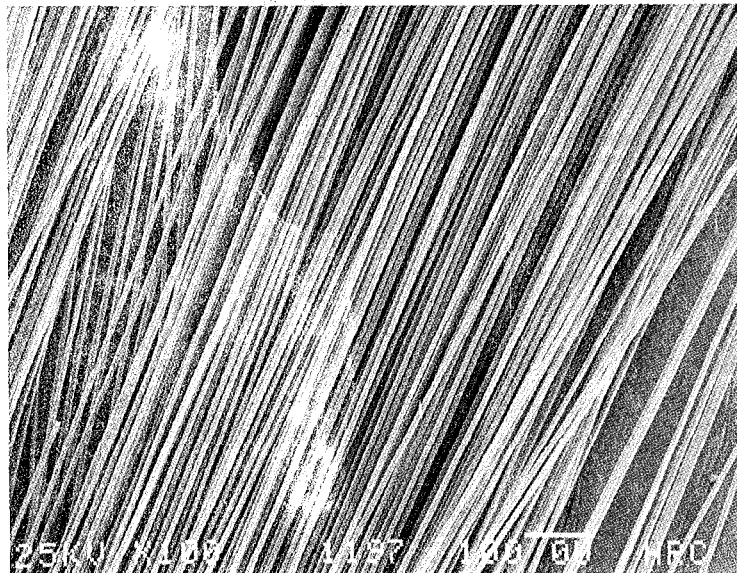
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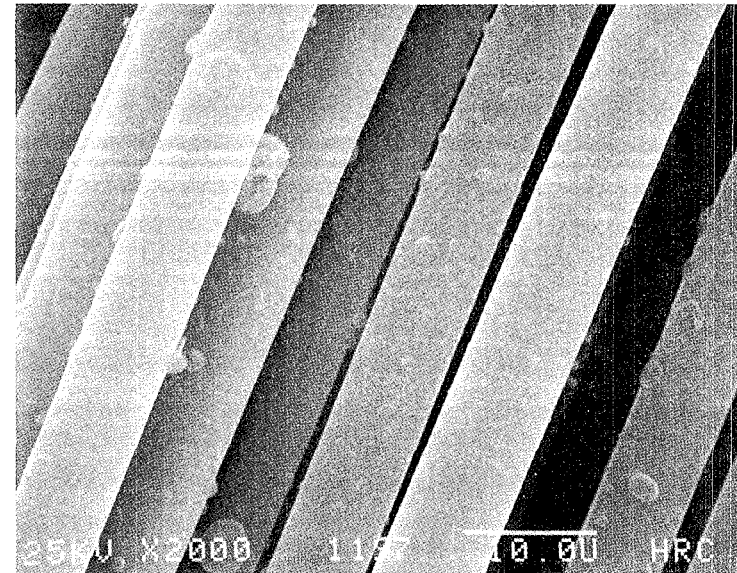
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X23033-25-1

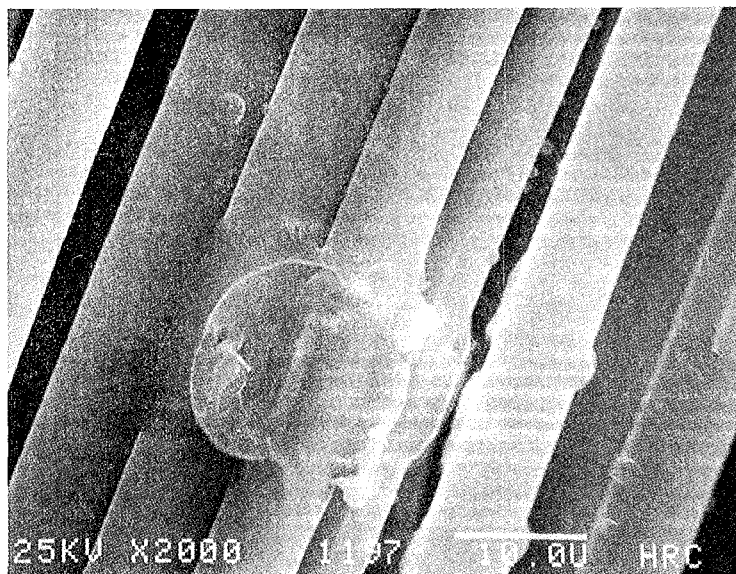
Figure 7—AS4P Fiber Treated With Surface Modified Styrene Latex at pH 6



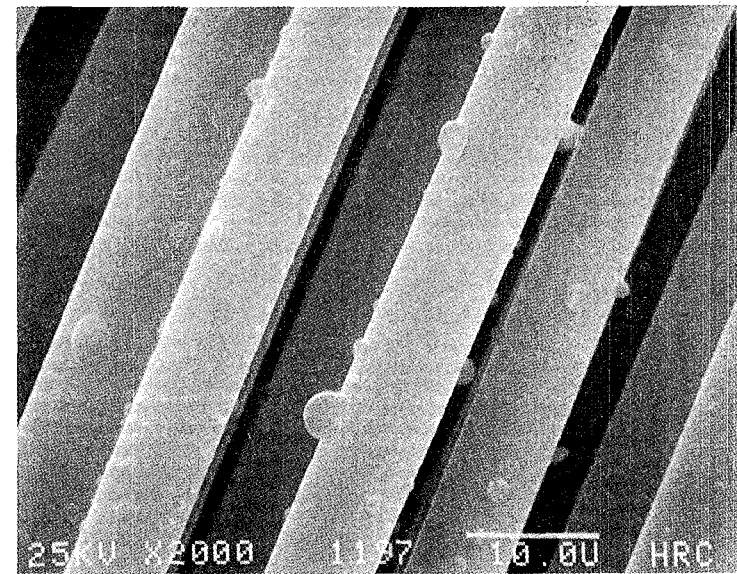
25-2a



25-2b

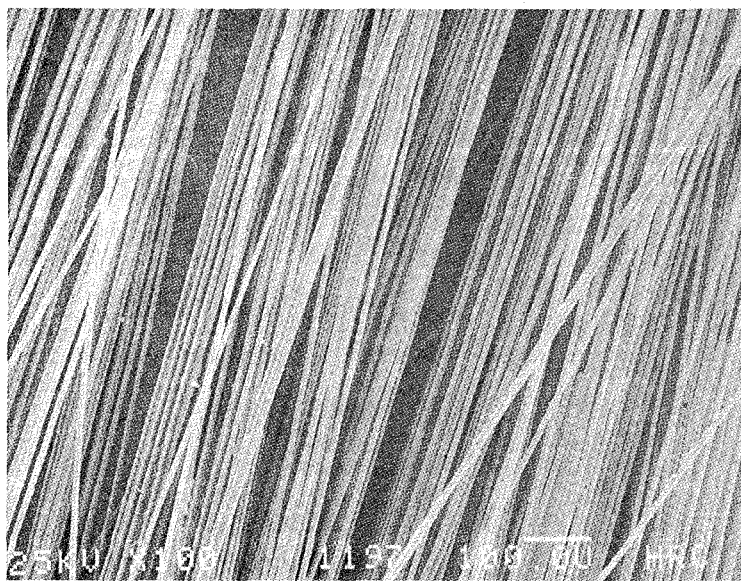


25-2c

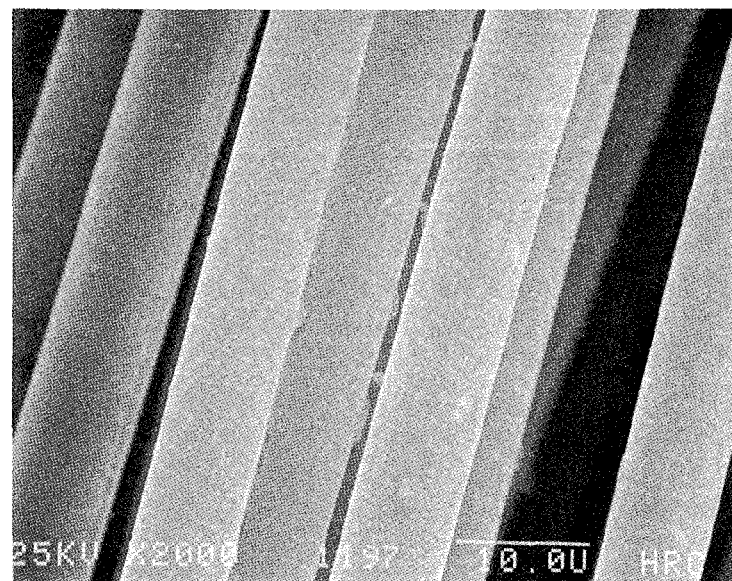


25-2d

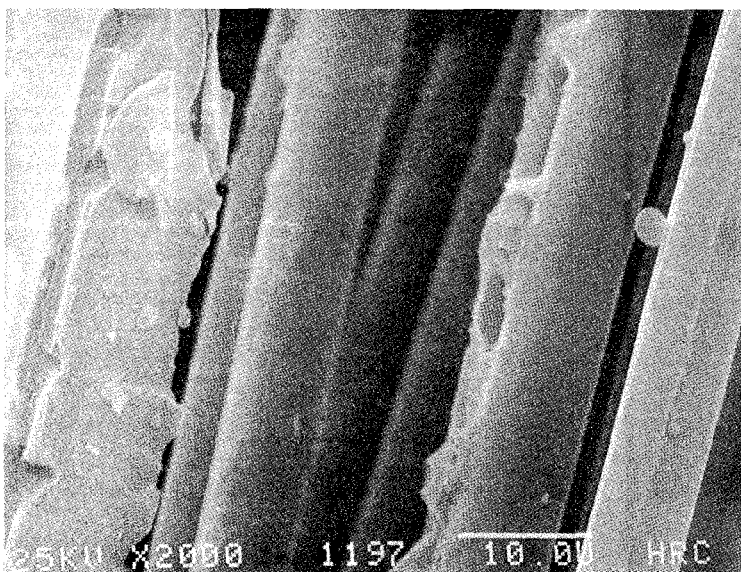
Figure 8— AU4 Fiber Treated With Epoxy Surface Modified Latex at pH 6



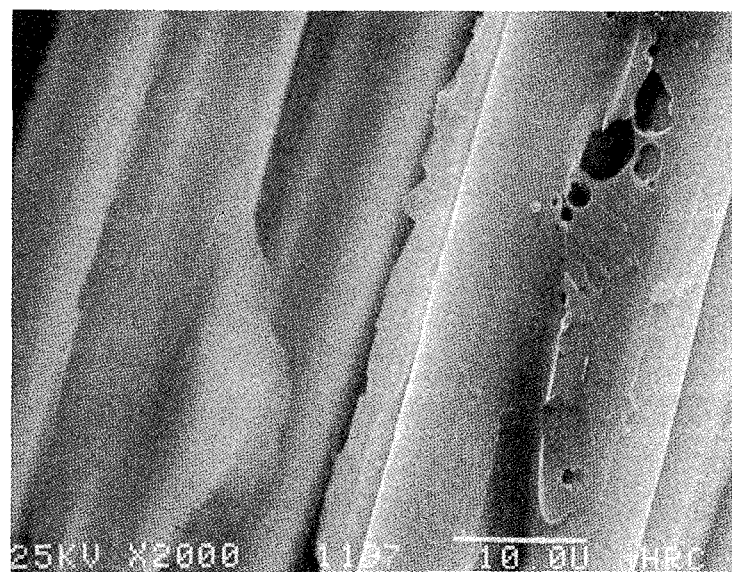
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25-3b



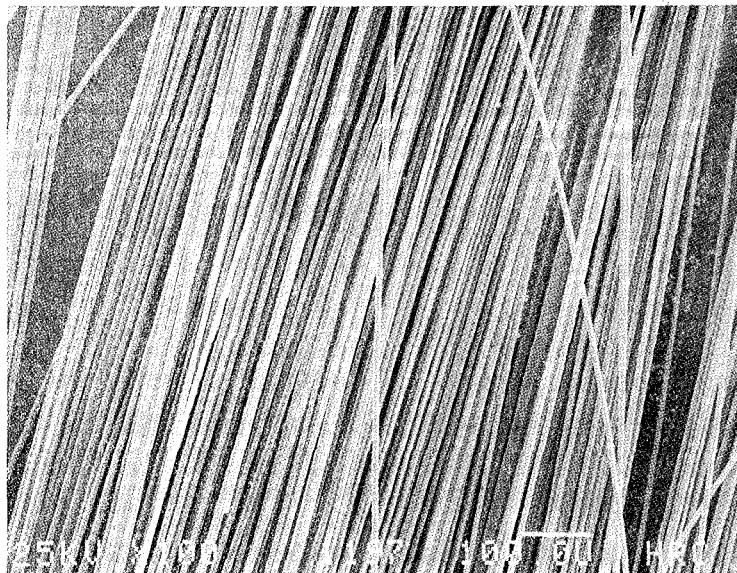
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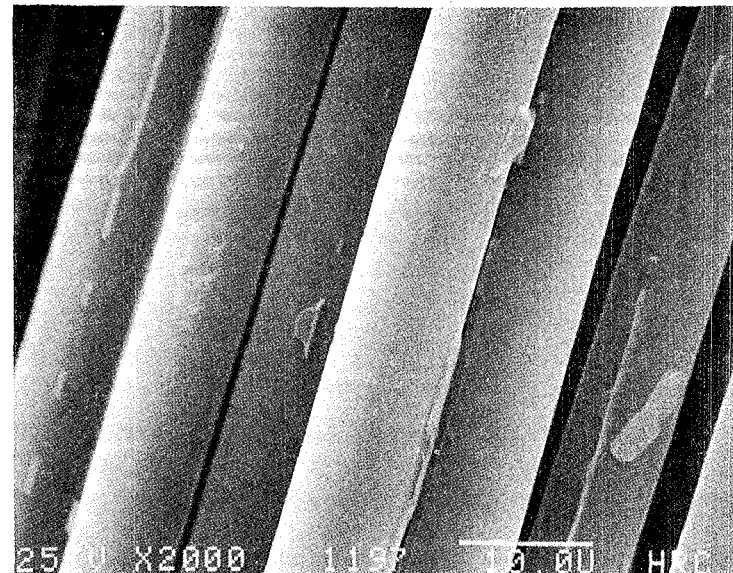
25-3d

X23033 - 25 - 3

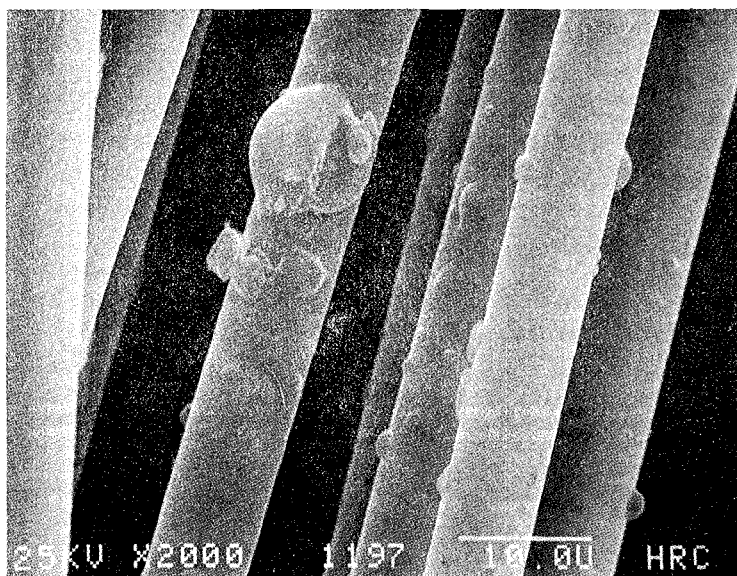
Figure 9—AS4P Fiber Treated With Epoxy Surface Modified Latex at pH 6



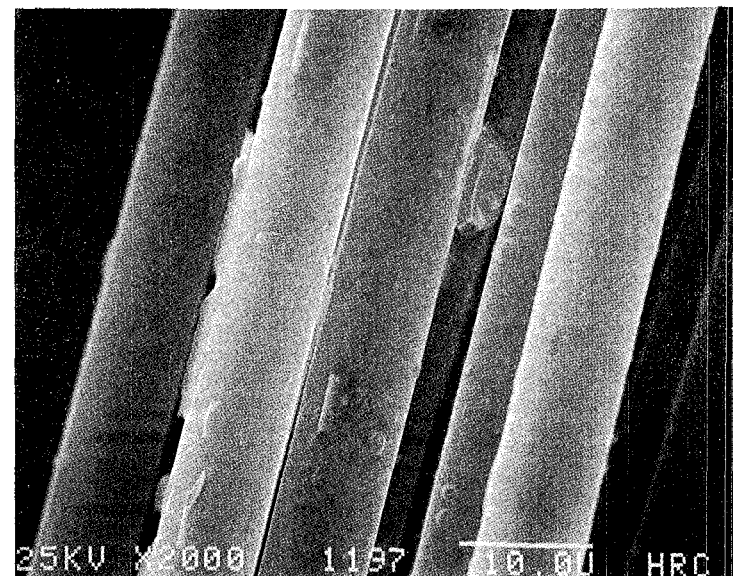
25-4a



25-4b



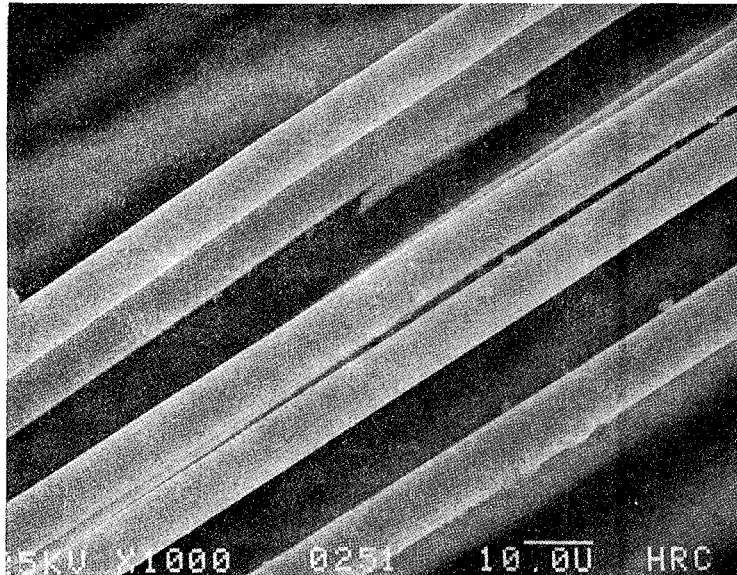
25-4c



25-4d

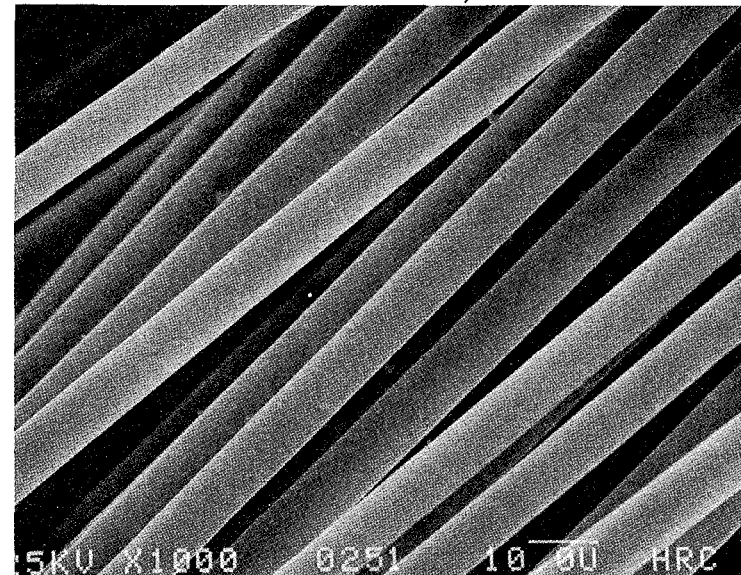
Figure 10—Epoxy Surface Modified Styrene Latex at pH 10

On AS4P
X23033-49-1

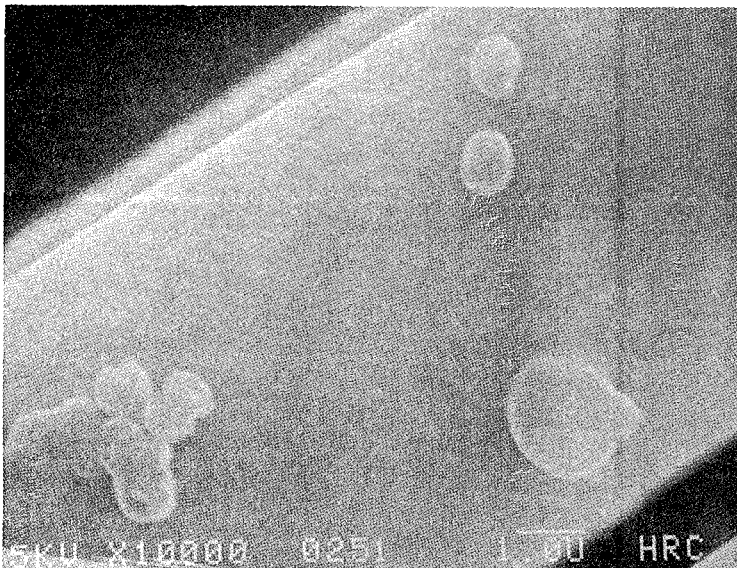


49-1a

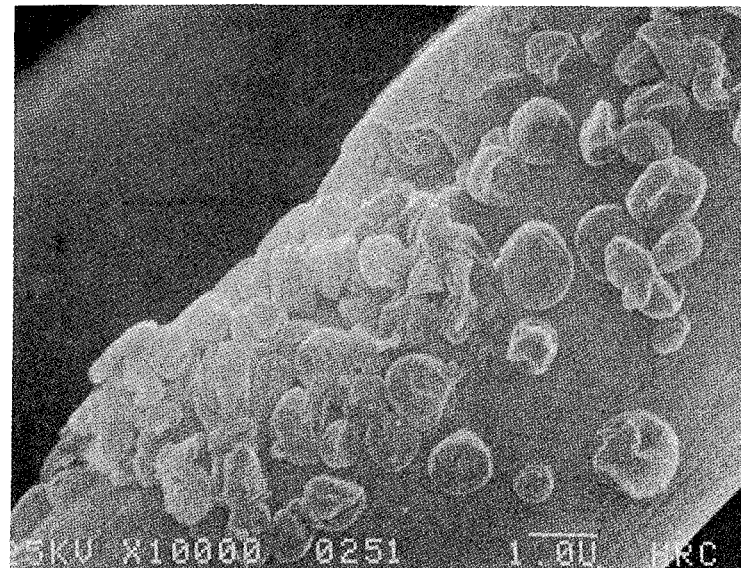
On AU4
X23033-49-2



49-2a



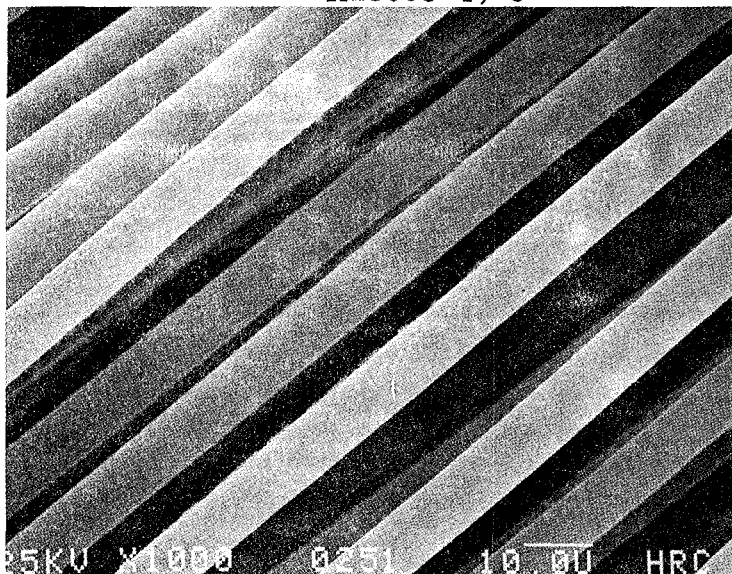
49-1b



49-2b

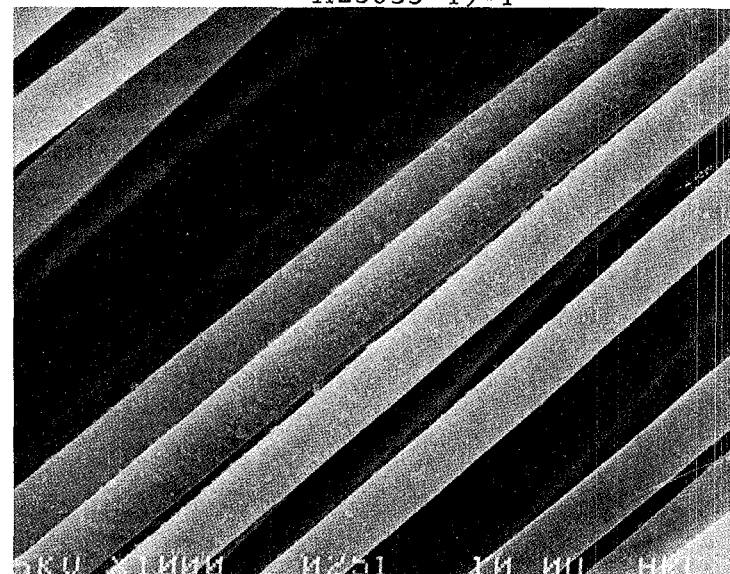
Figure 11—Epichlorohydrin-Modified Quat Latex at pH 10

On AS4P
X23033-49-3

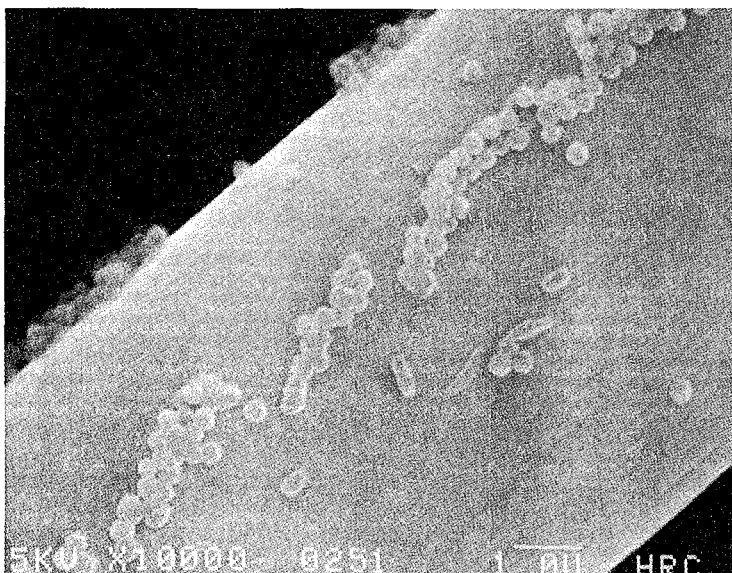


49-3a

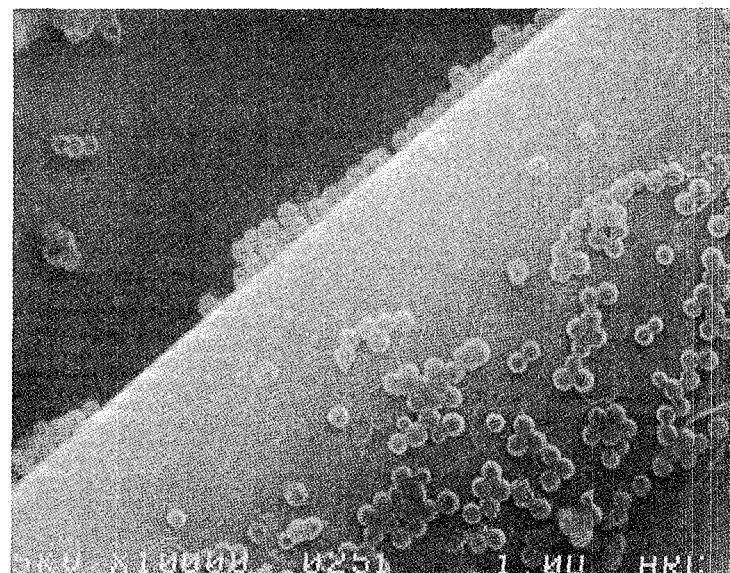
On AU4
X23033-49-4



49-4a

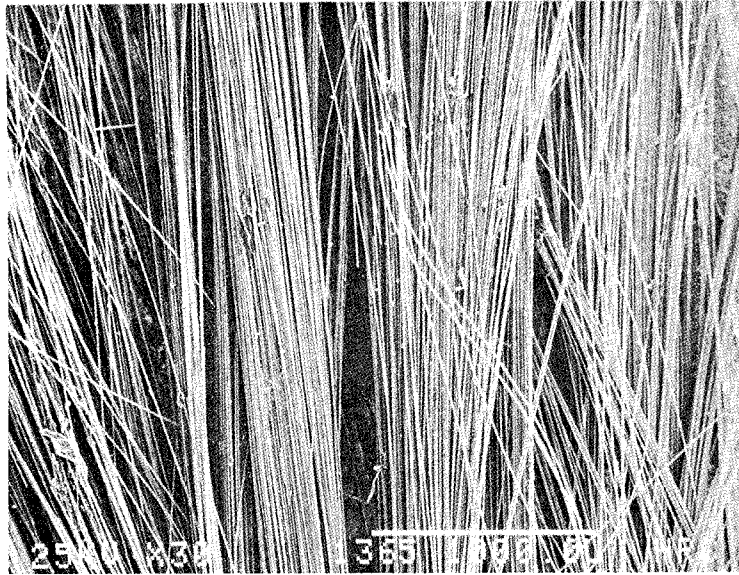


49-3b



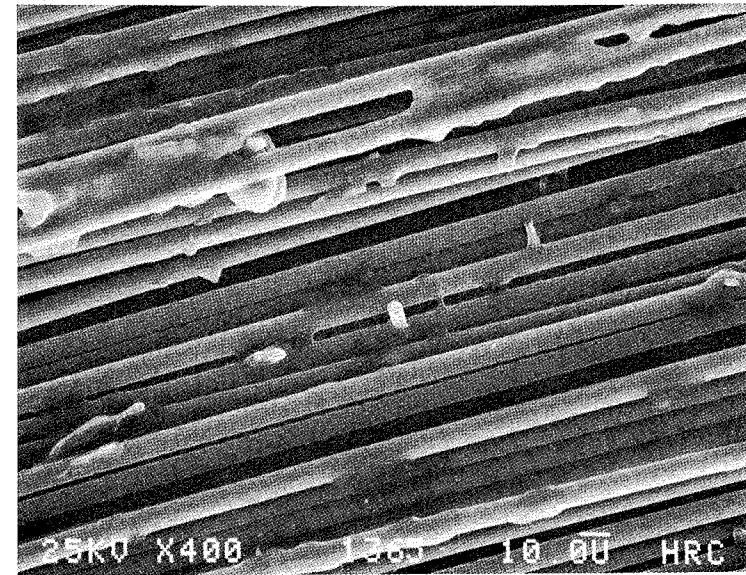
49-4b

Figure 12—AU4 Fiber Treated With Acrylic Rubber Latex at pH 10

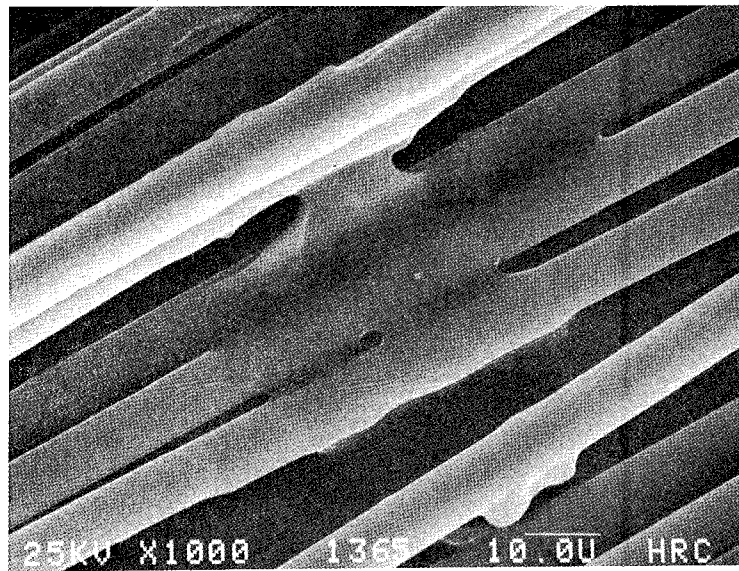


a

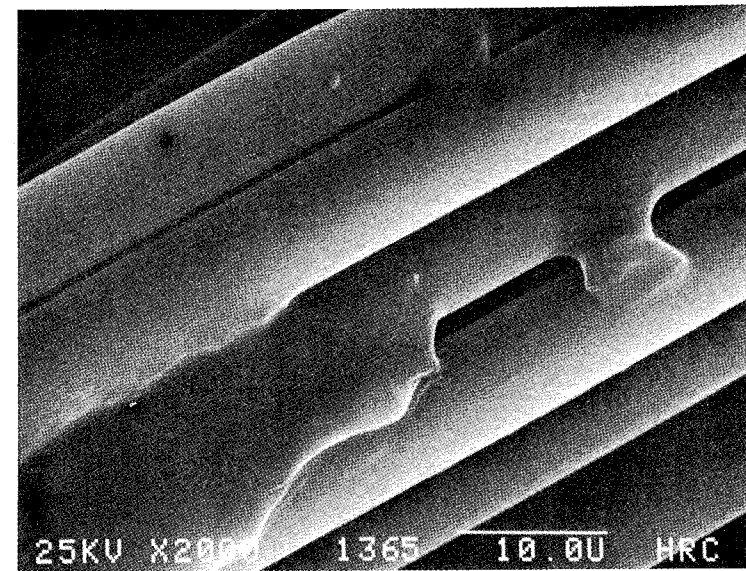
X23237-2A



b

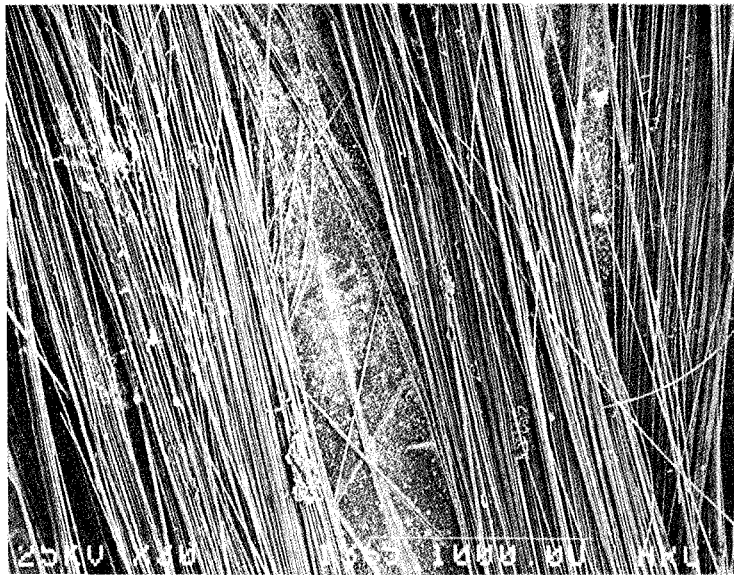


c

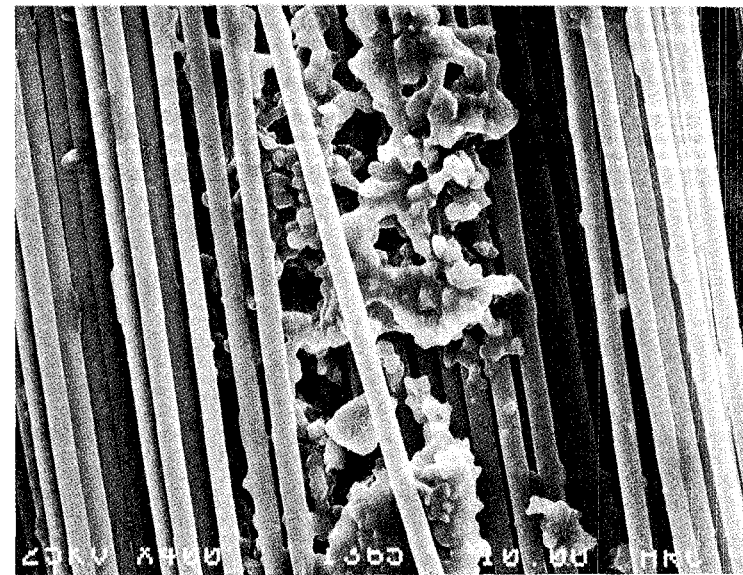


d

Figure 13—AS4P Fiber Treated With Acrylic Rubber Latex at pH 10



a



b

X23237-2B

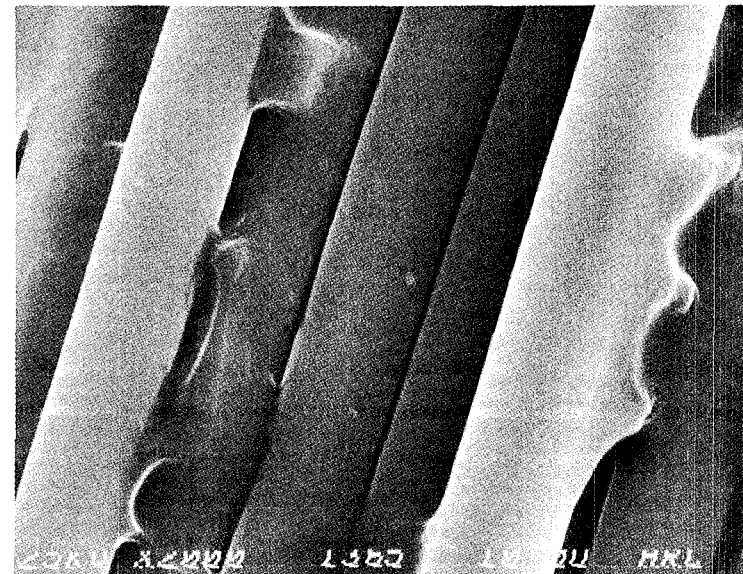
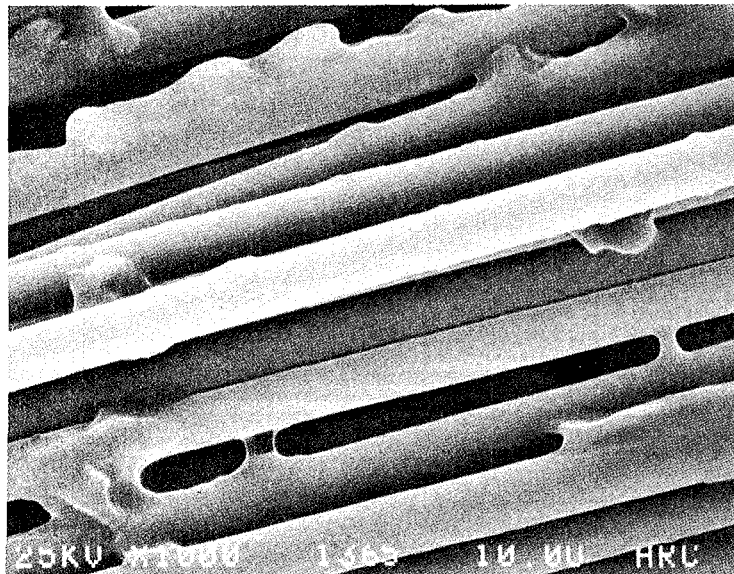
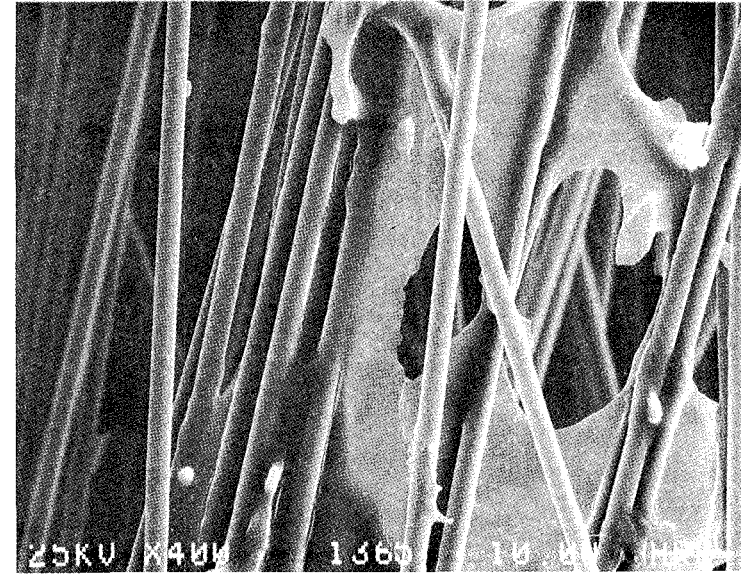


Figure 14—AU4 Fiber Treated With Acrylic Rubber Latex at pH 10 With Basic Wash

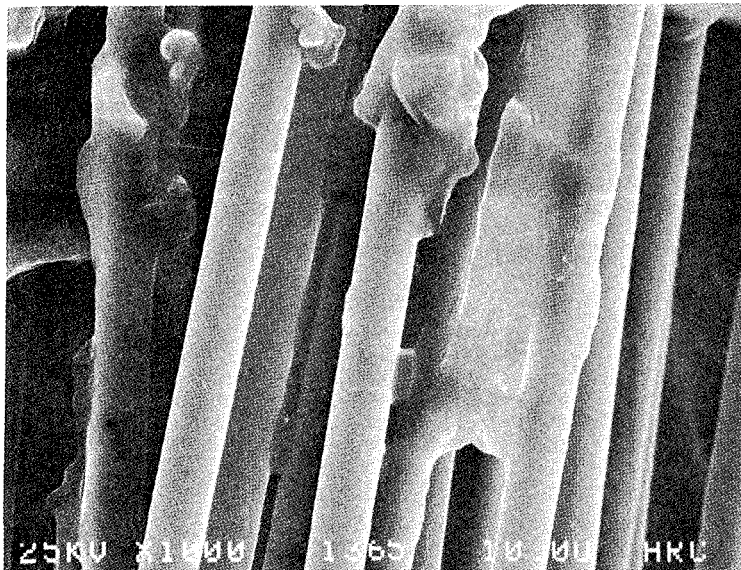


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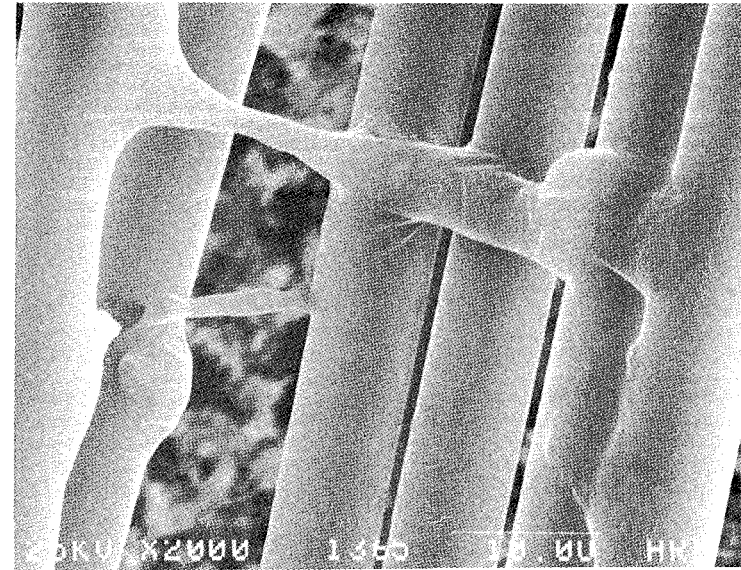


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16. Abstract Graphite (or carbon) fiber composite impact strength improvement was attempted by modifying the fiber surface. Elastomeric particles were made into latices and deposited ionically on surface-treated graphite fiber in an attempt to prepare a surface containing discrete rubber particles. With hard, nonelastomeric polystyrene discrete particle coverage was achieved. All of the elastomeric-containing latices resulted in elastomer flow and filament agglomeration during drying.					
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